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IMPINGER SOURCE SAMPLING METHOD FOR SELECTED ALDEHYDES, KETONES, AND POLAR COMPOUNDS

NCASI Southern Regional Center

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1.0 Introduction

1.1 Quality Assurance - This method shall be considered conducted only if all quality assurance procedures have been performed and all the results clearly reported in the sampling report. Sufficient data must be presented such that the QA results and calculations are transparent. A summary of QA procedures is provided in the appendix.

1.2 Caveats

This method has not been field validated via EPA Method 301 and is considered a self-validating method.

NCASI strongly suggests that sampling contractors and laboratories conduct train spikes and conduct full trial runs of all sample train configurations prior to use of this method in the field. Failure to do so will greatly increase the probability that quality assurance criteria will not be achieved.

NCASI recommends that mills, sampling contractors, and laboratories carefully review this method and all quality assurance procedures and criteria prior to source sampling. Since spikes will be used as one of the quality assurance procedures, evaluation of source concentration for the analytes of interest needs to be carefully undertaken prior to formulation of the spike solutions. If multiple and varied sources (for example, inlets and outlets of control systems) are to be sampled, multiple spike solutions or varied spike volumes will likely be necessary to meet spiking criteria.

This method was developed to sample the six compounds referred to as "Total HAPs" in the Plywood and Composite Wood Products MACT Rule (Subpart DDDD of 40 CFR Part 63, National Emission Standards for Hazardous Air Pollutants). These six compounds are methanol, phenol, acetaldehyde, acrolein, formaldehyde and propionaldehyde. The method should be capable of measuring a wider range of aldehydes, ketones, and polar organics. The method's fairly extensive quality assurance procedures will provide feedback on the methods ability to accurately measure a given compound.

1.3 Feedback

NCASI welcomes feedback on this method. Feedback on alternate sampling configurations, alternate lab and field techniques, alternate internal standards, sample handling procedures,

etc. will be appreciated. Feedback on the quality assurance criteria and procedures is also welcome, but keep in mind that this method is a self-validating method. Please submit feedback by e-mail to D_Word@src-ncasi.org.

1.4 Terminology

Procedural steps outlined by this method range from optional to mandated. Actions that are not to be performed are also specified. The following terms will be used within the text of this method in order to clarify these activities:

Term:	The action, activity, or procedural step is…
…must not….	Prohibited
…may…	Optional
…should…	Suggested
…must…	Required

1.4.1 Sample Batch – A grouping of samples.

1.4.2 mg/L - Milligrams per liter.

1.4.3 Sample Run – A sample collection period preceded and followed by quality assurance checks, such as flow rate measurements and leak checks, as specified in this method. The recommended sampling run duration is one hour. However other sample run times may be used if required by the specific sampling or source conditions. If very short or long sample runs are conducted, the minimum measurement level and the capacity of the BHA solution should be considered.

1.4.4 Sampling Event – Three or more consecutive sample runs conducted at a sample location or source type. The term "sampling event" is used in this method primarily with respect to quality assurance (QA) procedures or requirements.

1.4.5 Source Type – Used to describe emissions from a distinct process unit or a group of process units tested at a single location. For example, a rotary dryer and a press, each vented separately, are two distinct source types. Combined exhausts from a dryer and press sampled at a single location is a single source type.

1.4.6 Sample Location – An emissions sampling point or location. For the purposes of the field quality assurance requirements of this method, multiple emission points may be considered to be the same sample location if the emission characteristics (sample matrices) are similar. For example, an exhaust stream split so that it vents to two locations can be considered a single sample location. A press exhausted at three vents can be considered a single sample location. (Since the field quality assurance procedures for a self-validating method are primarily designed to assure the user that the sample method is valid for each source type or sample matrix

sampled, duplication of quality assurance procedures at a single source type with multiple, similar emission points is not required. For a three vent press, for example, only one duplicate sample run, and one run spike (or two bracketed run spikes) would need to be conducted for all three vents.) Note that this definition applies to the quality assurance procedures of this method only and does not imply that a single sample location can be used to adequately characterize a source's mass emission rate.

Control device inlets and outlets cannot be considered a single sample location with similar emission characteristics.

1.4.7 [AQU] – [AQU] indicates analytes in an aqueous matrix.

1.4.8 [HEX] – [HEX] indicates analytes in a hexane matrix.

1.4.9 Minimum Measurement Level (MML) – For this method, NCASI has established a MML of 0.4 mg/L for the [AQU] GC/FID analysis and 0.5 mg/L for the [HEX] GC/NPD analysis. This is a measurement level that all labs should be able to achieve for the six primary analytes: [AQU] methanol, phenol, [HEX] acrolein, acetaldehyde, formaldehyde, and propionaldehyde. Laboratories that wish to conduct a detection limit study and use lower detection limits may do so. Records of the detection limit study should be maintained.

1.4.10 Sampling System Minimum Measurement Level (SSMML) – For this proposed method, the SSMML is calculated based on the MML and source sampling parameters (sample volume, BHA solution volume, and hexane volume). The SSMML will, therefore, vary by sample run. An example is provided in the appendix.

1.4.11 Equivalency – This method allows labs and testers to use alternate procedures if equivalency is established. Equivalency may be established using the criteria provided in EPA Method 301 for paired sample systems ("Comparison with a Validated Method Using Paired Sample Systems"). For this comparison, assume the "Validated Method" is the procedure provided in this method. The proposed, alternative procedure is the "alternative test method." Follow the steps provided in Section 12.0 of EPA Proposed Method 301 (Federal Register, Vol. 69, No. 245, December 22, 2004, pages 76642-76655.

1.4.12 Second Source Standard - A second source or reference standard is a compound or material purchased from a different vendor than that used to prepare the primary stock solution or materials used to make the calibration curves. The second source standard provides a check on the reagents used to make the calibration curves.

2.0 Method ISS/FP-A.105.01

2.1 Principle and Applicability

This method was developed to capture six compounds termed "Total HAPs" in the PCWP MACT. These six compounds are comprised of two alcohols, methanol [67-56-1] and phenol [108-95-2], and four aldehydes, acetaldehyde [75-07-0], acrolein [107-02-8], formaldehyde [50-0-0], and propionaldehyde [123-38-6]. Theoretically, the method can capture a wide variety of aldehydes, ketones, alcohols, and other polar compounds. The method can be used for other compounds provided all QA criteria are met.

The field sampling equipment is relatively simple and very similar to the equipment used for NCASI Method CI/WP-98.01. Sample gas passes through three chilled aqueous impingers containing an o-benzylhydroxylamine (BHA) solution. The carbonyl group of aldehyde compounds reacts with the amine group of BHA forming aldehyde oximes and splitting off water. The alcohols are simply captured by the water and unaffected by the BHA. The aldehyde oximes have limited water solubility and form an emulsion in the bubbling impingers. The oximes may form a slight, somewhat oily layer at the water surface and may also coat the glass walls of the impingers.

The impingers and impinger contents are washed with hexane to extract the oximes. An aliquot of the hexane solution is introduced into a gas chromatograph with a nitrogen-phosphorous detector (GC/NPD) for quantification. The alcohols are determined by direct aqueous injection into a GC with a flame ionization detector (GC/FID).

Since this method contains self-validating procedures and criteria, the applicability is not restricted in terms of compounds or sources. The user must demonstrate the method's precision and accuracy on each source for each compound by conducting train spikes, run spikes, duplicate sample runs, and other procedures as required by the method.

This method is not appropriate for compounds that are insoluble in water or are slightly soluble in water (e.g., benzene). This method should only be used for water soluble compounds.

This method may be used for high moisture sources. But, extremely high moisture sources (greater than 90% moisture content, v/v) should be sampled with consideration to the volume of water that will be collected and the capacity of the BHA solution. Note that condensers, if used, will not contain BHA and the aldehydes captured in the condenser will not react with BHA until the condenser contents and the impinger solution are mixed in the sample bottle. Sufficient BHA must be available in the final mixture to derivitize the aldehydes and ketones.

This method should not be used on sources where significant amounts of entrained water droplets are present unless it is used in an isokinetic manner. There is potential, within the source ducts or stacks, for alcohols and aldehydes to concentrate in water droplets. Failure to capture a representative amount of water droplets can bias the results. Theoretically, isokinetic sampling will capture a representative portion of the water droplets. This method

may be used isokinetically if all QA/QC procedures are conducted and all QA/QC criteria are met. The flow rate to BHA solution volume ratio must be within the range discussed in Section 2.2.5, and care must be taken to avoid exceeding the capacity of the BHA solution. If the flow rate to BHA solution volume ratio exceeds 1000:1, it is recommended that train spikes be conducted prior to any field work and that the spiking solution be near or above the upper limits of the expected source. Additionally, BHA capacity calculations should be conducted.

Lab analyses must be conducted by or under the supervision of analysts experienced in the use of gas chromatographs and skilled in the interpretation of chromatograms.

2.2 Apparatus

This method allows substantial flexibility, but certain equipment or equipment operational parameters are mandated. Follow the nomenclature discussed in Section 1.4 (i.e., must, should, etc.) relative to field equipment, laboratory equipment and operational parameters. The sample train used in development of this method is based on NCASI Method CI/WP-98.01 and uses midget impingers and a critical orifice to regulate the sample flow rate. However, this method allows the use of alternative equipment and/or train configurations. For example, the midget impingers could be replaced with Greenburg-Smith design impingers or a dry gas meter could be used to measure sample gas volume. The following description, therefore, applies to the sample train as used by NCASI in Method CI/WP-98.01. Alternative configurations must incorporate components that will achieve the basic premise of the sample train design of filtering the sample gas stream at 250 ± 25°F followed by sample capture by the BHA solution in impingers.

2.2.1 Heated Sample Probe – The sample system must have a heated probe maintained at 250 ± 25°F. The probe must be constructed of stainless steel tubing or an equivalent inert material such as Teflon or glass.

2.2.2 Heated Filter Box – The sample system must have a heated filter box that is directly connected to the heated probe. The heated filter box must be maintained at 250 ± 25°F. The filter housing and connections may be made of stainless steel or an equivalent material, and the filter may be Teflon or an equivalent material. A thermocouple must be connected near or within the filter housing to record the filter housing or filter temperature. If two impinger trains are connected to one sample probe and heated filter box, the location at which the sample gas splits must be within the heated zone of the filter box. This filter box configuration would have an outlet connection for each impinger train.

2.2.3 Sample Line – An unheated Teflon line should be used to convey the sample from the back of the heated filter box to the first impinger. Care should be taken to avoid any condensation within the filter box, including insulating the connections at the heated box/unheated Teflon line junction.

2.2.4 Impingers – The sample line must be connected to three or more chilled impingers in series in an ice or ice/water bath. The impingers should have regular tapered stems or equivalent. All impinger train connectors should be glass and/or Teflon. The impinger size is not specified by this method, allowing midget impingers to large impingers. A condenser may be used prior to the first impinger, but all liquid and rinse from the condenser must be composited with the impinger liquid sample. Additionally, an impinger containing silica gel or another drying agent may be used after the three BHA impingers. This impinger and its contents do not have to be evaluated for capture of the compounds of interest.

2.2.5 Sample Flow Rate and Impinger Solution Volume – The ratio of sample gas flow through the impingers to the initial BHA solution volume (both expressed as milliliters) must be between 200:1 to 4000:1 (e.g., 30,000 mL of sample gas through the three impingers containing a total of 75 mL of BHA solution = 400:1). Note that this is a very wide ratio range. At the upper ratios, sampling companies should conduct calculations to evaluate the ability of the BHA solution to derivitize the aldehydes expected from the source (BHA capacity calculations). A general 'rule of thumb' is that no more than 10% of the capacity of the derivitizing solution should be used. However, since this is a self-validating method, sampling companies may exceed the 'rule of thumb' at their own risk. Sampling companies should conduct train spikes, before going into the field, to demonstrate that the sampling train can operate effectively at the upper ratios with the highest level of emissions expected in the field.

NCASI's work with this method has been conducted using three small impingers containing 75 mL of BHA solution and operating at a sampling rate of 500 mL/minute for one hour.

2.2.6 By-pass Valve – A by-pass valve may be located downstream of the flow rate control device (e.g. critical orifice) to alleviate the need to turn off the sample pump during off-line periods such as during leak checks or standby periods.

2.2.7 Variable Area Flow Meter – A flow meter should be placed in line after the impingers for a flow check during sampling.

2.2.8 Flow Control Device – A calibrated critical orifice or equivalent device should be used to maintain a steady flow rate through the collection train. Sample flow rate may be established by the use of a critical orifice and pre- and post-flow measurements. Also, the total sample flow may be established by a dry gas meter.

2.2.9 Vacuum Gauges – To provide a visual verification during a sample run that the flow through the critical orifice remains critical, two vacuum gauges should be placed on each side of the critical orifice capable of reading 25 inches of mercury gauge (in. Hg).

2.2.10 Vacuum Pump – The critical orifice must be followed by a pump or other device to pull the sample gas through the impingers. The pump or device must be capable of providing a vacuum of about 18 inches of mercury and must be able to maintain critical conditions at the orifice (a difference in pressure of about 15 inches of mercury). Other equivalent systems to insure steady-state flow through the impingers may be used, but these systems **must** be described in the report along with a discussion of their ability to maintain steady-state flow.

2.2.11 Thermometer – A calibrated thermometer is used to measure the ambient temperature.

2.2.12 Barometer – A calibrated barometer is used to measure atmospheric pressure.

2.2.13 Sample Bottles – Samples must be stored in glass bottles with Teflon-backed lids or equivalent lids. Plastic or other non-glass sample bottles cannot be used.

2.2.14 Laboratory Glassware and Supplies

2.2.14.1 Separatory funnels

2.2.14.2 Autosampler vials capable of holding 2 mL

2.2.14.3 Volumetric flasks

2.2.14.4 Volumetric pipets

2.2.14.5 Syringes

2.2.15 Analytical Equipment – Equipment in this section (all of Section 2.2.15) should be used unless equivalency is established. Records of equivalency must be maintained. Although detectors other than NPD could be used for detection of oximes in hexane, it is strongly suggested that laboratories use an NPD and mandatory that an equivalency test be conducted for any other detector used. Records of such an equivalency test must be maintained. Deviations from the use of a NPD must be recorded in the test report.

2.2.15.1 [AQU] GC System - GC analytical system with a purged packed injection port. A split/splitless injection port may be used if equivalency is established, but the MML and SSMML for methanol and phenol must be considered (see appendix).

2.2.15.2 [AQU] Guard Column - 10 m x 0.53 mm deactivated fused silica capillary column.

2.2.15.3 [AQU] Column – 60 meter or longer x 0.53 mm x 3 μm, 6% cyanopropylphenyl, 94% dimethylpolysiloxane bonded phase (624 phase) fused

silica capillary column (e.g., J&W Scientific DB-624, Hewlett Packard HP-624). Other columns may be used if equivalency is demonstrated.

2.2.15.4 [AQU] GC Detector - Flame ionization detector with appropriate data system.

2.2.15.5 [HEX] GC System - GC analytical system with split/splitless injection port.

2.2.15.6 [HEX] Guard Column - 10 m x 0.53 mm deactivated fused silica capillary column.

2.2.15.7 [HEX] Column - 30 m x 0.25 mm x 0.25 μm film RTX-200 fused silica capillary column (Restek or equivalent) or other column shown to be capable of resolving the analytes of interest.

2.2.15.8 [HEX] GC Detector – Nitrogen phosphorus detector (NPD) with appropriate data acquisition system.

2.3 Reagents

2.3.1 Chemical Quality - Reagent grade compounds or the highest purity available must be used.

2.3.2 DI Water - Deionized water quality is verified in the [AQU] GC/FID blanks.

2.3.3 [AQU] Primary Internal Standard – Cyclohexanol [108-93-0] or 2,2,2-trifluoroethanol [75-89-8].

2.3.4 [HEX] Primary Internal Standard –Nitrobenzene [98-95-3].

2.3.5 [HEX] Surrogate Standard – Methoxypropanone [5878-19-3] may be used as a surrogate standard.

2.3.6 Hexane - Hexane must be used to rinse the impingers in the field and extract the samples in the laboratory. Hexane should be reagent grade or better. Alternate extraction solvents may be used only after equivalency has been established.

2.3.7 Isopropanol and Methylene Chloride – Isopropanol and methylene chloride are used to wash the impingers and separatory funnels between samples. Isopropanol removes left over water and methylene chloride removes the isopropanol and any residual hexane and allows rapid drying. Reagent grade or better methylene chloride and isopropanol should be used. Equivalent, less toxic, substitutes for methylene chloride may be used but hexane and isopropanol must be soluble in the substitute solvent.

2.3.8 o-Benzylhydroxylamine – o-Benzylhydroxylamine is purchased as o-benzylhydroxylamine hydrochloride (BHA-HCl). This chemical should be reagent

grade or better. o-Benzylhydroxylamine (BHA) sampling solutions are made by dissolving 30 grams of BHA-HCl in a liter of DI water. (Note that the solubility is about 40 to 50 grams per liter at lab temperatures). Care should be taken to prevent ambient sources of aldehyde from reacting with the BHA solution. Keep the solution sealed and refrigerated.

A liter aqueous solution containing 30 grams of BHA is 188 millimolar. At a sampling ratio of 200:1 (see Section 2.2.5) this solution has a capacity to sample a gas stream of about 22,500 ppmvd of formaldehyde (assuming formaldehyde is the only aldehyde or ketone in the gas stream). For a ratio of 1000:1 the capacity is reduced to about 4,500 ppmvd of formaldehyde. This system should not be operated at levels approaching full capacity. A "rule of thumb" is no more than 10% of capacity. Since the method is a self-validating method, sampling companies may operate at conditions exceeding the 'rule of thumb' at their own risk.

2.3.9 [AQU] Primary Aqueous Internal Standard – Cyclohexanol [108-93-0], 2,2,2-trifluoroethanol [75-89-8], or an equivalent compound can be used as the internal standard.

2.3.9.1 [AQU] Cyclohexanol Internal Standard Solution – Prepare the aqueous [AQU] internal standard primary spiking stock solution by adding 3.12 mL cyclohexanol to a tared 100 mL ground glass stoppered volumetric flask filled to approximately 90 mL with DI water, taking care to inject the cyclohexanol directly into the water. Weigh the flask after the addition of the cyclohexanol and record the weight to the nearest 0.1 mg. Fill the flask to 100 mL with DI water. Assuming 100% compound purity, this will result in a nominal 30,000 mg/L [AQU] internal standard primary spiking stock solution. Compute the exact concentration (mg/L) using the weight gain and actual purity. The solution can be stored at room temperature for up to 6 months.

2.3.9.2 [AQU] 2,2,2-Trifluoroethanol Internal Standard Solution – Prepare the aqueous [AQU] internal standard primary spiking stock solution by adding 2872 μL of 2,2,2-trifluoroethanol to a tared 100 mL ground glass stoppered volumetric flask filled to approximately 90 mL with DI water, taking care to inject the 2,2,2-trifluoroethanol directly into the water. Weigh the flask after the addition of the 2,2,2-trifluoroethanol and record the weight to the nearest 0.1 mg. Fill the flask to 100 mL with DI water. Assuming 100% compound purity, this should result in a nominal 40,000 mg/L [AQU] internal standard primary spiking stock solution. Compute the exact concentration (mg/L) using the weight gain and actual compound purity. This solution must be stored in a refrigerator and held no longer than 6 months.

2.3.10 [HEX] Hexane Internal Standard Solution – Nitrobenzene [98-95-3] or an equivalent compound can be used as the internal standard.

2.3.10.1 [HEX] Preparation of the Hexane Internal Standard – Prepare the hexane based [HEX] internal standard primary spiking stock solution by

adding 1672 µL of pure nitrobenzene to a tared 100 mL ground glass stoppered volumetric flask filled to approximately 90 mL with hexane, taking care to inject the nitrobenzene directly into the hexane. Weigh the flask after the addition of the nitrobenzene and record the weight to the nearest 0.1 mg. Fill the flask to 100 mL with hexane. Assuming 100% compound purity, this should result in a nominal 20,000 mg/L [HEX] internal standard primary spiking stock solution. Compute the exact concentration (mg/L) using the weight gain and actual purity. This solution must be stored in a refrigerator and held no longer than 12 months.

2.3.11 [AQU] Alcohol Primary Stock Solution – Fill a 100 mL ground glass stoppered volumetric flask to approximately 90 mL with DI water. Tare the flask after the addition of the water. Using a syringe or equivalent device, add 126 µL of methanol, taking care to inject the methanol directly into the water. Weigh and record the weight gain to the nearest 0.1 mg. Add 100 mg phenol. Weigh and record the weight gain to the nearest 0.1 mg. Fill flask to the mark. Assuming 100% purity, this will result in a nominal 1,000 mg/L methanol and 1,000 mg/L phenol primary stock solution. Use the weight gain and the compound purity to compute the exact compound concentrations. An alternative would be to purchase a primary stock solution from a chemical reference supply company. The primary stock solution must be stored in the refrigerator and must be re-prepared monthly. The storage time of sealed or nitrogen blanketed standard solutions has not been evaluated at this time. Longer storage time may be allowed in cases where data are provided that supports it.

2.3.11.1 Alcohol Calibration and Matrix Spike Solutions – Prepare calibration standard solutions by dilution of the calibration primary stock solution using syringes or volumetric pipettes to measure the required aliquots of primary standard. The required dilutions are shown below. Prepare matrix spike solutions by calculating the concentration of analytes desired and diluting the primary stock solution.

µL of Stock Solution to Add to 10 mL Volumetric Flask	Resulting Methanol and Phenol Concentration, (mg/L)
1,000	100
500	50
250	25
100	10
50	5
10	1
4	0.4

2.3.12 Aldehyde Primary Stock Solution – Fill a 100 mL ground glass stoppered volumetric flask to approximately 90 mL with DI water. Tare the flask after the addition of the water. After each addition of analyte, weigh and record the weight gain to the nearest 0.1 mg. Using a syringe or equivalent device, add 127 µL of acetaldehyde, taking care to inject the acetaldehyde directly into the water. In a like manner, add 119 µL acrolein, 250 µL formalin, and 126 µL of propionaldehyde. Once all the analytes have been added, fill the flask to the mark. Assuming 100% compound purity and exactly 37% formaldehyde in the formalin, this will result in a nominal 1,000 mg/L acetaldehyde, 1,000 mg/L acrolein, 1,000 mg/L formaldehyde, and 1,000 mg/L propionaldehyde. Use the measured weight gains and actual compound purity to compute the exact analyte concentrations.

Note that acetaldehyde and propionaldehyde are extremely volatile and degrade as compounds over time. Acrolein, while less volatile, degrades as a neat compound and in aqueous solutions. A chilled (freezer temperature) gas-tight syringe should be used to deliver the neat compounds to the volumetric flask. Acrolein and acetaldehyde are also best kept in a freezer and measured at freezing temperatures. The syringe and neat compounds should be approximately the same temperature. New neat compounds or standards for acetaldehyde, acrolein, and propionaldehyde should be obtained when the second source standard requirement is not met using freshly prepared standards. An alternative would be to purchase a primary stock solution from a chemical reference supply company. The formalin solution should be checked to verify the actual formaldehyde concentration. Also, the formalin solution contains methanol at approximately 12% for stability and solubility purposes. This quantity of methanol should be considered for any instance in which the aldehyde and alcohol standards or spike solutions are mixed.

The aldehyde primary stock solution must be stored in the refrigerator and must be re-prepared monthly. The solution may need more frequent preparation for acrolein. The storage time of sealed or nitrogen blanketed standard solutions has not been evaluated at this time. Longer storage time may be allowed in cases where data are provided that supports it.

2.3.12.1 Aldehyde Calibration and Matrix Spike Solutions – Prepare calibration standard solutions by dilution of the calibration primary stock solution using syringes to measure the required aliquots of primary standard. The required dilutions are shown below. Prepare matrix spike solutions by calculating the concentration of analytes desired and diluting the primary stock solution.

µL of Stock Solution to Add to 10 mL Volumetric Flask	Resulting Formaldehyde, Acetaldehyde, Acrolein, and Propionaldehyde Concentration (mg/L)
1,000	100
500	50
250	25
100	10
50	5
10	1
5	0.5

2.4 Quality Assurance Procedures and Requirements – Laboratory and Field Testing

2.4.1 Laboratory Quality Assurance Procedures and Requirements

2.4.1.1 GC Maintenance

2.4.1.1.1 [AQU] [HEX] Injector Maintenance – The septum and injection liner should be replaced when necessary. If this is not done, retention time shifts and peak broadening can occur.

2.4.1.2 GC Performance and Quality Assurance Requirements – This section provides quality assurance (QA) procedures that must be conducted by the laboratories unless otherwise specified. The results of these procedures must be compared to the QA criteria and clearly reported. Sufficient data must be presented such that the QA results and calculations are transparent.

2.4.1.2.1 [AQU] [HEX] Laboratory Blank Sample – One method blank must be prepared per analytical batch to demonstrate that all materials are interference-free, and must be analyzed prior to further analyses. The concentration of the analytes in the blank should be below 0.5 mg/L for the [HEX] samples and below 0.4 mg/L for the [AQU] samples. Blank samples must include the appropriate internal standard.

2.4.1.2.2 [AQU] [HEX] GC Calibration Verification Standard – The calibration verification standard shall be the mid-range calibration standard. This calibration check must be performed prior to analysis of the sample batch, after every 10 source samples analyzed, and at the end of the sample batch. A calibration check is conducted to verify that the GC system is operating within acceptable parameters. The concentrations of the

analytes should be within ±15% of the expected concentrations. Additionally, the response (peak area) of the verification standard should be within 30% of the peak area of the mid-range calibration standard and the peak area of the internal standard should be within 30% of the mean peak areas of all calibration standards. For example, if a 50 mg/L mid level standard for methanol had a peak area of 60,000 and the cyclohexanol internal standard mean peak area was 30,000, the calibration verification standard should have an analytical value between 42.5 and 57.5 mg/L, a methanol peak area between 42,000 and 78,000 and a cyclohexanol peak area between 21,000 and 39,000.

If the criteria are not met, the GC system may require maintenance. If routine maintenance does not correct the problem, a new standard prepared from a fresh calibration stock solution should be run. If this still fails, the instrument will need to be recalibrated.

2.4.1.2.3 [AQU] [HEX] Laboratory Duplicates – One laboratory duplicate of a source sample must be analyzed. Additional laboratory duplicates must be analyzed for every 10 source samples analyzed. Duplicates are a replicate sample analysis of the same source sample. The percent difference of the duplicate concentrations should be within 20%. Percent difference is calculated as the difference between the two samples divided by the average of the two samples.

2.4.1.2.4 [AQU] [HEX] Matrix Spike Recovery (optional) – A matrix spike may be prepared for each batch of samples. Using the mean concentration determined by the replicate analyses or the level determined from a single measurement, determine the spiking level which will give 0.5 to 10 times the sample concentration. If the sample does not have detectable levels of analytes, spike the sample at approximately five times the lowest calibration level of the instrument. Spike the sample with the determined amount of the calibration standard/matrix spike solution and analyze the sample in the normal manner.

Calculate the percent recovery using Equation 2.1.

Equation 2.1

$$R = \left(\frac{C_S - C_N}{C_T} \right) \times 100$$

Where:

R = percent recovery of matrix spike
C_S = measured concentration of spiked sample
C_N = measured concentration of native sample
C_T = theoretical concentration of spike

2.4.1.2.5 [AQU][HEX] Second Source or Reference Standard – Analysis of a second source or reference standard is required for each analyte for each batch of samples. The reference standard should be approximately the same concentration as the calibration verification standard. The percent recovery of the second source standard should be 70 to 130%. If it is not, the lab should prepare a new standard or perform instrument maintenance. If necessary, recalibrate the instrument.

In the case of aldehyde or ketone oximes, a second source standard may be unavailable. If unavailable, a second source standard may be made in the lab from aldehydes or ketones purchased from a source other than the one from which the calibration standards, or calibration materials, were purchased.

2.4.2 Field Testing Quality Assurance Procedures – This section provides quality assurance (QA) procedures that must be conducted. The results of all these procedures must be compared to the criteria and clearly reported in the test report. Sufficient data must be provided such that the QA results and calculations are transparent.

Users of this method are required to implement the field testing quality assurance procedures in this section. Quality assurance measures are conducted prior to, during, and/or after field testing to provide a means of evaluating the quality of sampling conducted. Note that this method also requires laboratory quality assurance procedures as covered in the above Section 2.4.1.

The field quality assurance procedures for this method require: (1) a field blank, (2) a duplicate sample run, (3) a run spike(s), (4) a train spike, and (5) the associated field spikes for each sampling event at each sample location (defined in Section 1.4). These field quality assurance procedures are defined in this section and criteria are specified where applicable. Further, this method establishes criteria for the level or relative magnitude of the spikes, termed "equivalent spiking level," as defined in Section 2.4.2.1.

The field quality assurance procedures are somewhat complicated and need to be planned well in advance of arriving at the facility to conduct testing. As indicated in the introduction to this method, it is strongly suggested that two qualification train spike runs be conducted in the sampling company's office or laboratory prior to any

field work. Furthermore, laboratory trials of the duplicate and run spikes should be conducted prior to actual testing to acclimate the sampling crew(s) to the requirements of this method.

2.4.2.1 Equivalent Spiking Levels – All spikes introduced into the sample trains, either as a train spike (Section 2.4.2.6) or run spike (Section 2.4.2.5), have an "equivalent spiking level." This is defined as the compound concentration that would result if the spike were present in a dry standard gas (air) of the same volume as the sample gas volume of the spiked sample trains as shown in Equation 2.2. For example, assume a spiked sample train operates at a dry standard flow rate of 500 mL per minute for one hour (30 liters, total) and a 1 mL spike is introduced that contains 100 mg/L (μg/mL) of methanol. 100 μg of methanol in 30 liters of gas yields an equivalent spiking level of 2.50 ppmvd of methanol. This is a theoretical, calculated concentration in air - not a measured concentration.

Equation 2.2

$$ESL_{ppmvd} = \frac{(\mu g\ Field\ Spike)(24.04)}{(L\ SampleVol_{spiked\ train})(Cmpd.MW)}$$

Where:

ESL = Equivalent Spiking Level
μg Field Spike = μg of Compound in Field Spike
L Sample $Volume_{spiked\ train}$ = Liters of Sample Volume for Spiked Train
Cmpd. MW = Compound Molecular Weight

Ideally, the spike solution used for single run spikes would yield an equivalent spiking level that matches the source concentration for each compound. This, of course, is impossible. But, efforts should be made to match the equivalent spiking level to the source gas concentration. This method sets criteria for equivalent spiking levels for single run spikes and bracketed run spikes. Labs and/or sampling companies should estimate the source concentrations for every compound to be sampled at every source, and a spike solution should be formulated for each source that provides equivalent spiking levels near the source concentrations. Equivalent spiking levels that are very small relative to the source concentration make it very difficult to obtain good spike recoveries. Equivalent spiking levels that are very large relative to the source concentration make it easy to obtain a good spike recovery but do not necessarily demonstrate sampling proficiency. For this reason, NCASI has established criteria for equivalent spiking levels for this method. This method also allows bracketed spikes intended to help the user for cases in which the source concentration cannot be closely estimated.

The verification of an equivalent spiking level used for a particular sample event can only be accomplished after the run spike results have been compiled. For a run spike, the results provided by the non-spiked (or normal) impinger train will determine the *actual* source gas concentration for a targeted compound. The equivalent spiking level will be calculated using the results from analysis of the field spike and the gas sample volume of the spiked sample train. (The mass of compound in the field spike, determined from lab analysis, is used as the spiked mass for calculation of the equivalent spiking level.)

To check whether an equivalent spiking level meets the method criteria for a **single run spike**, select the appropriate concentration range in the left column of Table 2.1, then determine the maximum equivalent spiking level allowed for that concentration range as indicated in the right column of the table. The equivalent spiking level for a single run spike compound must be within the specified limits.

For **bracketed run spikes** the equivalent spiking level criteria are provided in Table 2.2. Bracketed run spikes are discussed in Section 2.4.2.5.3.2.

Table 2.1 Single Run Spike Criteria for Equivalent Spiking Levels

If the *actual* source gas concentration of a targeted compound is…..	Then the equivalent spiking level for that targeted compound must be at or greater than the sample system minimum measurement level and….
…less than 0.5 ppmvd	….. no more than 2 ppmvd.
…between 0.5 to 1.5 ppmvd	….. no more than 6 ppmvd.
…is greater than 1.5 ppmvd	….. no more than four times the source concentration.

Table 2.2 Bracketed Run Spike Criteria for Equivalent Spiking Levels

Spiking Level	Criterion
Low Equivalent Spiking Level	Should be less than the source gas concentration. Must be no more than 5 times the actual source gas concentration, in order to be used in the spike recovery calculation
High Equivalent Spiking Level	Must be less than or equal to 10 times the actual source gas concentration, in order to be used in the spike recovery calculation

2.4.2.2 Field Blank – There must be at least one field blank per facility or

mill tested. The field blank is simply a sample bottle containing the BHA sampling solution. This bottle is taken out to the field, labeled, opened, hexane is added, and then it is handled along with the other sample bottles. The field blank must be extracted and analyzed along with the other samples collected by this method and the results reported in the source sampling report. NCASI recommends that one field blank be prepared per day so that more than one blank is available for analysis.

2.4.2.3 Duplicate Sample Run or Duplicate - One duplicate sample run must be conducted per sampling event at each sampling location (see Section 1.4.6 – a "location" may include more than one emission point). A common sampling configuration used to conduct a duplicate sample run will be to connect two separate impinger trains to a single probe and filter box. Two complete sampling trains may also be used. Alternative configurations for conducting a duplicate sample run can be used if the duplicate sample run criteria are met.

2.4.2.3.1 Notes Regarding Duplicate Trains – (1) Leak checks of duplicate trains are a common source of field error. Make sure that the impinger trains are isolated prior to leak checks. (2) Both impinger trains for a duplicate sample run should start and end the sample run at approximately the same time. (3) The results from duplicate sample trains must be reported as an average according to Section 2.4.2.3.2.

2.4.2.3.2 Reporting Results from Duplicate Sample Trains – The results from the two sample trains are averaged and reported. If either or both sampling trains are below the SSMML, the results should be reported according to the applicable regulation or as required by the applicable regulatory authority. The sampling report should include the individual results from the two trains in the report's QA/QC section.

2.4.2.3.3 Calculation of Percent Difference for a Duplicate Sample Run – Calculate the difference between the source gas concentration obtained from the two sample trains and divide by the average concentration as shown below. Note that the masses of the compounds collected in the two trains are not compared.

$$\%\,difference = Abs\left|\frac{Train1_{ppmvd} - Train2_{ppmvd}}{Average\left(Train1_{ppmvd}, Train2_{ppmvd}\right)}\right|$$

The percent difference is not calculated for cases in which the

compound concentration from one or both impinger trains is below the SSMML.

2.4.2.3.4 Duplicate Difference Criteria – Calculate the source gas concentration for each of the targeted compounds from the duplicate sample trains and determine the applicable duplicate difference criteria shown in Table 2.3. Clearly report the percent difference and compare it to the applicable criteria for each compound and for each sample event. Sufficient data must be presented such that the calculations are transparent.

Table 2.3 Duplicate Criteria

If the average source gas concentration for the duplicate sample run is….	Then the duplicate difference should be…...
…less than 0.5 ppmvd	…..equal to or less than 50%
…between 0.5 to 1.5 ppmvd	….equal to or less than 40%
…greater than 1.5 ppmvd	….equal to or less than 30%

2.4.2.4 Field Spike – Prepare one field spike for each run spike and train spike. The field spike is important because the mass collected in a spiked impinger train will be compared against the mass in the field spike for spike recovery purposes.

A field spike must be collected during or immediately after a run spike or a train spike. To collect a field spike, select an unused sample bottle containing BHA sampling solution and record the bottle ID and weight information on the field sheet used for the spiked QA sample run (or equivalent). Inject the same spike volume used for the run spike into the field spike sample bottle. Seal the container and allow it to sit at ambient temperature for 15 minutes or place in an ice chest or refrigerator for one hour. Add hexane to the sample bottle in an amount equivalent to the amount of hexane used for the impinger rinse of the spiked train (Section 2.5.2). Store and handle this sample with the other samples for analysis.

2.4.2.5 Run Spike – The run spike quality assurance requirement can be met by conducting either (1) a single run spike or (2) a bracketed run spike for each sampling event. For the run spike, a spike solution is introduced into one of the two impinger trains (referred to as the spiked train) to determine if the spiked mass can be recovered. The solution spiked into the sample train must meet the equivalent spiking level criteria (Section 2.4.2.1). Run spike recovery criteria are provided in Table 2.4.

Table 2.4 Spike Recovery Criteria

If the Actual Source Concentration is…..	Spike Recovery Range…..
…less than 0.5 ppmvd	…should be between 50 and 150%
…between 0.5 to 1.5 ppmvd	…should be between 60 and 140%
…greater than 1.5 ppmvd	…should be between 70 and 130%

A common sampling configuration used to conduct a run spike will be to connect two separate impinger trains to a single probe/filter box. Two complete sampling trains may also be used. Alternative configurations for conducting a run spike can be used if the spike recovery criteria can be met.

Note that for the run spike, the figure in the appendix shows that the spiked train is equipped with a spiking tee at the inlet to the first impinger. Alternatively, the spiking solution can be introduced into the impinger prior to beginning the run (but before the leak check). Note, however, that relatively slow introduction of the spiking solution during the sample run more closely emulates sampling conditions and may increase the chances of a successful spike recovery. NCASI recommends slow introduction of the spike solution by syringe through a tee and septa during the first 10 to 30 minutes of the run spike.

2.4.2.5.1 Notes Regarding Run Spikes – (1) Single run spikes must meet the equivalent spiking level criteria in Table 2.1. (2) The criteria for bracketed run spikes are more complicated (Table 2.2 and Section 2.4.2.5.3.2). (3) Each run spike must have an associated field spike (Section 2.4.2.4). (4) The spiked and non-spiked (referred to as "normal") sample trains and associated samples should be separately labeled and named. (5) Like duplicates, trains must be isolated during leak checks (Section 2.5.8.1). (6) Run spikes evaluate both accuracy and precision and, therefore, are typically more difficult than train spikes and duplicates. (7) The source gas concentration for a run spike will be based on the result obtained from the normal (non-spiked) impinger sample train.

2.4.2.5.2 Spike Recovery Calculation – The percent recovery calculation for the run spike has three basic steps. (1) The compound concentration obtained from the normal train is subtracted from the compound concentration obtained from the spiked train. (2) The resulting concentration difference is then multiplied by the gas sample volume of the spiked sample train (with appropriate conversion factors) to obtain the mass of the spike that was recovered. (3) The mass recovered is divided by the mass spiked and expressed as a percent recovery as shown in Equation 2.3.

Equation 2.3

$$Net\ Mass\ Recovered_{[i]} = \left(Concentration_{spiked\ train[i]} - Concentration_{normal\ train[i]}\right) \times Sample\ Volume_{spiked\ train\ std[i]}\ x\ Conversion\ Factors$$

$$Spike\ Recovery_{[i]} = \frac{net\ mass\ recovered_{spiked\ train[i]}}{mass_{field\ spike[i]}}$$

For example, assume the normal sample train and spiked sample train have methanol concentrations of 2.5 and 5.5 ppmvd, respectively. Also, assume the spiked train had a dry standard sample volume of 30 liters and that 100 µg of methanol was spiked into the spiked train ($mass_{field\ spike}$) as determined from the field spike. The concentration difference between the two trains is 3.0 ppmvd. Multiplying the 3 ppmvd value by 30 liters and applying appropriate conversion factors yields a $mass\ recovered_{spiked\ train}$ of 120 µg of methanol. The final spike recovery is 120/100 * 100 = 120%. Note that the mass in the normal train cannot be subtracted from the mass of the spiked train (in the first step) because the two sample trains do not typically have the same sample volumes.

An alternative, simple, but perhaps less intuitive, means of calculating the spike recovery is shown in Equation 2.4.

Equation 2.4

$$Spike\ Recovery_{[i]} = \frac{\left(Concentration_{spiked\ train_{[i]}} - Concentration_{normal\ train_{[i]}}\right)}{ESL_{[i]}}$$

Where:

ESL = Equivalent Spiking Level (Section 2.4.2.1)

A spike recovery is not calculated for a targeted compound if the *actual* source gas concentration for that compound is measured below the SSMML in the normal impinger train.

2.4.2.5.3 Spike Recovery Criteria – This method provides two options for run spikes: (i) the single run spike and (ii) the bracketed run spike. The spike recovery result from either of these procedures should be compared to the criteria in Table 2.4. The

spike recovery results must be compared to the criteria and clearly reported. Sufficient data must be presented such that the results and calculations are transparent.

2.4.2.5.3.1 Single Run Spike – If a single run spike is conducted, the spike must meet the equivalent spiking level criteria provided in Table 2.1 and the spike recovery should meet the criteria in Table 2.4. The single run spike should be conducted when the user is familiar with the source and expected analyte concentrations. If the user cannot estimate the analyte concentrations of the source gas, bracketed run spikes are recommended.

2.4.2.5.3.2 Bracketed Run Spikes – This section provides rules for calculating the spike recovery from bracketed run spikes. The bracketed run spike is used when the concentration of the source gas at a source type is variable or not easily estimated. For this option, two run spikes will be required for each sample event.

A low level run spike should be conducted at a low equivalent spiking level anticipated to be *below* the *expected* source gas concentration but above SSMML for the targeted compound.

The high level run spike should be conducted at a high equivalent spiking level anticipated to be *above* the *expected* source gas concentration, but no more than 10 times the source gas concentration.

The following **rules** must be used for calculating the spike recovery for the bracketed run spike option:

Rule 1. If the low equivalent spiking level is determined to be greater than 5 times the *actual* source gas concentration and the high equivalent spiking level is less than or equal to 10 times the *actual* source gas concentration for a targeted compound, then the *high* level run spike is used in determining the spike recovery.

Rule 2. If the low equivalent spiking level is equal to or less than 5 times the actual source gas concentration, and the high equivalent spiking level is greater than 10 times the *actual* source gas concentration for a targeted

compound, then the *low* level run spike is used in determining the spike recovery.

Rule 3. If the low equivalent spiking level is less than or equal to 5 times the source concentration and the high equivalent spiking level is less than or equal to 10 times the *actual* source concentration for a targeted compound, then calculate the following four parameters:

(3a) The spike recovery of the low level run spike.

(3b) The percent difference in the low spike equivalent spiking level and the actual source gas concentration as shown in Equation 2.5.

Equation 2.5

$$LSPD = \frac{|LESL - C_A|}{C_A} x100$$

Where:

LSPD = low spike percent difference (absolute value)
LESL = low equivalent spiking level
C_A = actual source gas concentration

(3c) The spike recovery of the high level run spike.

(3d) The percent difference in the high spike equivalent spiking level and the actual source gas concentration as shown in Equation 2.6.

Equation 2.6

$$HSPD = \frac{|HESL - C_A|}{C_A} x100$$

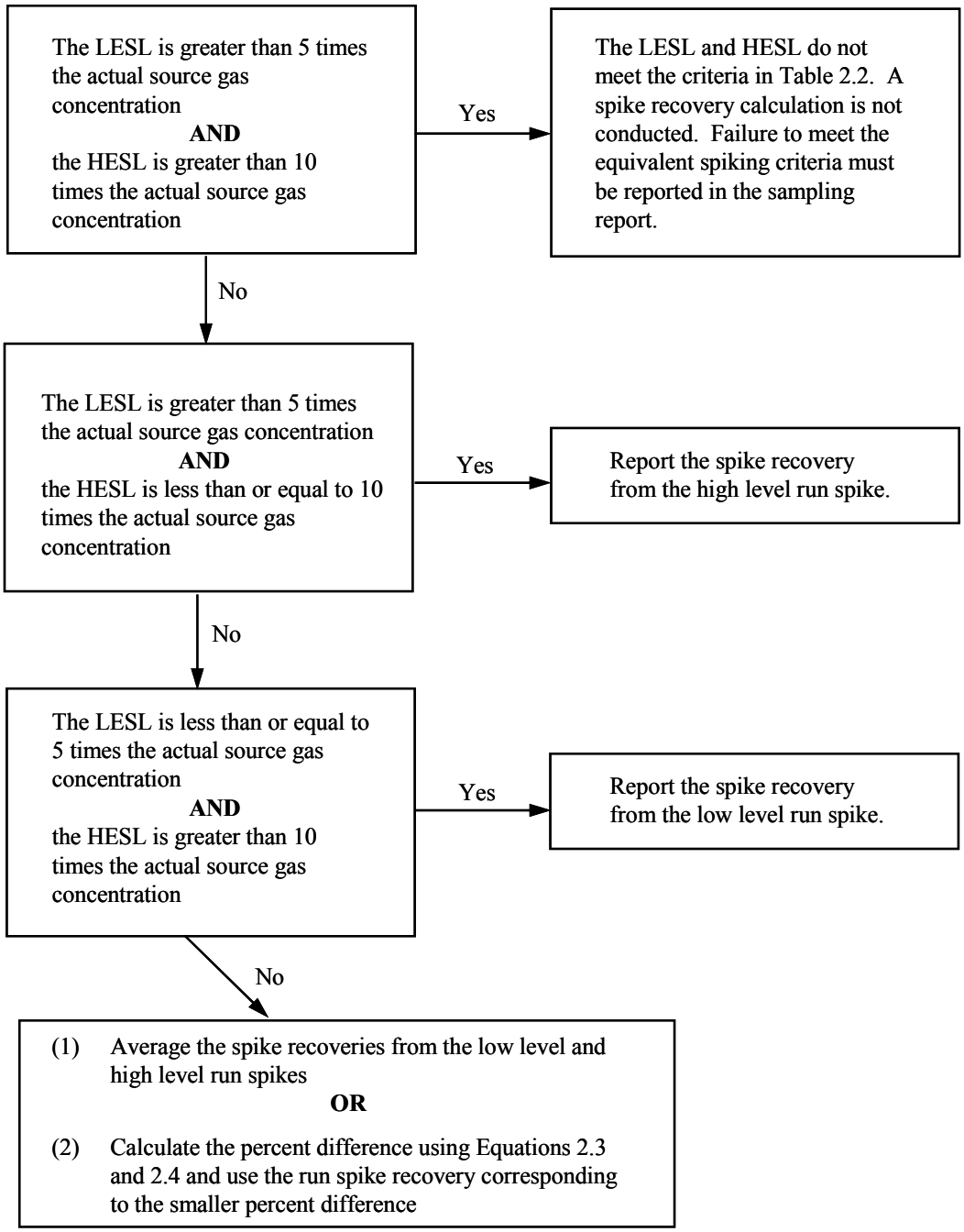
Where:

HSPD = high spike percent difference (absolute value)
HESL = high equivalent spiking level
C_A = actual source gas concentration

The spike recovery for **Rule 3** is based on the following two options: (i) the average of the spike recoveries determined in 3(a) and 3(c) above **OR** (ii) the spike recovery corresponding to the smallest percent difference determined in 3(b) and 3(d) above. The user may pick the option that provides the better spike recovery value. If the average spike recovery option is used, the actual source gas concentration, for the purposes of evaluating the spike recovery criteria (Table 2.4), will be the average of the two normal sample trains.

Rule 4. If the low equivalent spiking level is determined to be more than 5 times the actual source gas concentration and the high equivalent spiking level is greater than 10 times the actual source gas concentration, the equivalent spiking levels do not meet the criteria in Table 2.2. In this case, a spike recovery calculation should not be conducted and a spike recovery should not be reported. The report, however, must state that the sampling company failed to meet the equivalent spiking level criteria.

Figure 2.1 provides a flow diagram intended to help the user understand the bracketed spike recovery rules. Additionally, the appendix contains a worksheet and example calculation.



HESL – high equivalent spiking level
LESL – low equivalent spiking level

Figure 2.1 Bracketed Spike Recovery Rules

2.4.2.5.3.3 Example for a Bracketed Run Spike – A three run set on a source consisted of a duplicate, a high run spike, and a low run spike. The *normal* sample train from both spiked sample runs provided a source gas concentration of 10 ppmvd of methanol (considered the *actual* methanol concentration).

The low equivalent spiking level for the low run spike was 4 ppmvd. The spike recovery for the low run spike was 65%. Since 4 ppmvd is less than 5 times the actual source gas concentration, the low spike percent difference was calculated to be:

$$\frac{|4-10|}{10}\times 100 = 60\%$$

The high equivalent spiking level was 30 ppmvd for the high run spike. The spike recovery for the high run spike was 90%. Since 30 ppmvd is less than 10 times the *actual* source gas concentration, the high spike percent difference was calculated to be:

$$\frac{|30-10|}{10}\times 100 = 200\%$$

The bracketed run spike recovery for the source in this example could be based on either the (i) average of the low and high spike recoveries (77.5%) or (ii) the spiked sample train with the lower percent difference, which provided a spike recovery of 60%. Assuming the sampling company chooses to use the 77.5% spike recovery, this value is assessed against the criteria in Table 2.4 and the sample set is shown to meet the spike recovery criteria.

2.4.2.6 Train Spike – The primary purpose of the train spike is to evaluate the entire sampling train's sampling accuracy. (Note that the run spikes, which are spiked in the first impinger, do not evaluate the potential for compound loss in the probe and filter box.)

One train spike must be conducted for each mill visit. This QA procedure can be conducted prior to source testing, while in the field, or after source testing.

However, this procedure must be conducted within 7 days of the first or last day of the mill sampling or mill visit.

Each compound evaluated by the train spike must be spiked at an equivalent spiking level above the detection limits but no more than 5 ppmvd.

The train spike will be conducted using only one collection train attached to the heated probe and filter box as shown in the appendix. This collection train will be operated outside or independent of the source(s) tested. The spike is injected into the probe tip of the collection train.

If desired, the train spike can be configured using two impinger trains operating in parallel behind a single heated probe and filter box. Note that the spike recovery for each impinger train is expected to be half that of a single impinger train, so spike volumes or concentrations may need to be adjusted for this configuration.

2.4.2.6.1 Train Spike Notes – (1) Care must be taken to prevent introduction of any ambient organic contaminants during this procedure. Charcoal sorbent tubes placed at the probe tip to treat the ambient air entering the measurement system will minimize bias due to contamination. (2) Care should also be taken to inject the spike solution far enough into the heated probe to ensure complete volatilization of the aqueous spike. (3) The spike should be introduced over a 10 to 30 minute time period because a single quick injection may cause poor spike recovery. (4) The train spike must be operated for the same time period (usually one hour) and sample flow rate that is expected to be used during source sampling.

2.4.2.6.2 Train Spike Recovery - The spike recovery is determined by dividing the mass collected in the spiked train by the mass measured in the associated field spike. The spike recovery is reported as a percent.

$$\text{Spike Recovery}_{[i]} = \frac{\text{mass}_{\text{spiked train}[i]}}{\text{mass}_{\text{field spike}[i]}}$$

2.4.2.6.3 Train Spike Criteria - The spike recovery criteria for the train spike is 70% to 130%. These criteria are not concentration dependent but the equivalent spiking level must be less than 5 ppmvd.

2.5 Procedure

It is imperative that all users of this method first thoroughly read the entire method prior to executing any field testing. An understanding of both the required reagents (Section 2.3) and the quality assurance procedures (Section 2.4) is necessary to execute this method. The following procedures are written primarily for a sampling system much like the one used for NCASI Method CI/WP-98.01 but an attempt has been made to allow substantial flexibility. The following procedures will need to be altered for other sample trains. The user should, however, comply in some manner with the intent of the following procedures.

2.5.1 Preparation of the BHA Sample Bottles – Determine the volume of aqueous BHA sampling solution required for each sample run (Sections 2.3.8 and 2.2.5). Select a sample bottle that has sufficient capacity to accommodate the BHA solution volume plus rinse and condensate that will be collected during sampling. Record the sample ID and tare weight (sample bottle with cap and label) for each sample bottle. Add the required BHA solution to each sample bottle and record the pre-sample weight of each bottle. Alternative procedures for measuring or tracking the volumes of the [AQU] and [HEX] samples may be used; however, the final volumes must be accurate.

2.5.2 Preparation of Hexane Rinse Bottles – This method requires a rinse of the impingers with hexane after sample collection. The hexane used in the rinse will also be used for the first of the three extractions. The sampling company may want to prepare an additional set of bottles containing known quantities of hexane for the impinger rinses. Alternative procedures for measuring or tracking the volumes of the [AQU] and [HEX] samples may be used; however, the final volumes must be accurate.

Since this method allows for different impinger sizes, the volume of hexane rinse is not specified. The amount of hexane to be used in the rinse must conform to the following rules:

1. A minimum of one milliliter of hexane must be used for every 12 mL of BHA solution initially used in the impingers.

2. The amount of hexane rinse used should be approximately one-third of the total amount of hexane used for extraction of the sample (Section 2.5.11).

After determining the volume of hexane rinse required for a representative sample run, select a container that has sufficient capacity to accommodate this volume of hexane or three times this volume if the bottle is to be re-used for the lab sample. Record the ID and tare weight (bottle with cap and label) for each bottle. Add the required volume of hexane to each sample bottle and record the new weight of each bottle. Alternative procedures are allowed, but the volume of hexane used in the rinse must be tracked and recorded.

2.5.3 Field Data Sampling Sheet – Each sample run must have a field sheet that documents pertinent information concerned with field testing this method. (An example is provided in the appendix.)

2.5.4 Preparation of the Spike Solution – The aqueous spike solution will consist of the appropriate concentration of each targeted compound in DI water. The spike solution should result in 'equivalent spiking levels' (Section 2.4.2.1) that meet the criteria in Tables 2.1 and 2.2.

2.5.4.1 Verification and Handling of Spiking Solution – The spiking solution and spike addition procedures may be the most common sources of spike recovery failure. NCASI suggests that all spiking solutions be analyzed and quantified for verification after formulation on the same instrument(s) that will analyze the samples (if possible). This should be done before the spikes are taken into the field to address any gross differences in the formulas (theoretical values) and measured values. Similarly, it is strongly recommended that some of the spiking solution should be returned to the lab after the field trip and again analyzed. This will provide information on degradation of the spike solution during the field trip. The spike solution must be kept on ice or refrigerated from the time of formulation until all sampling and analysis are complete.

For convenience, 2 mL GC vials with no headspace can be used to transport and store the spike solutions. If the GC vials are used, then the laboratory should retain one (or more) vials for an analysis record of each unique spike solution formulated. Furthermore, one GC vial for each unique spike solution should be retained from the batch of spikes sent to the field for the analysis record.

One milliliter is a convenient spike volume if GC vials are used. A syringe needle inserted through the vial septum will allow air to enter the vial during extraction of the spike with a separate needle and syringe.

2.5.5 Selection of the Equivalent Spiking Level – Criteria are established for the equivalent spiking level in Sections 2.4.2.1 and 2.4.2.5.3.2, thus it is important that an appropriate equivalent spike level for a particular source type or sample location is chosen. Run spike criteria are established for "single run spikes" and "bracketed run spikes." The criteria are more lenient for bracketed run spikes, but two run spikes must be conducted rather than one.

2.5.6 Preparation of Collection Train – The probe and filter housing must be cleaned with DI water or alternative cleaners and the filter replaced prior to testing each new source type or sample location. All unheated sample lines must be cleaned by rinsing thoroughly with DI water. The impingers must be cleaned according to Section 2.5.10.7. If an empty impinger or other vessel is to be used as a condenser prior to the first BHA impinger, then rinse the condenser with DI water. Replace the

silica gel or drying impinger at the end of the impinger train as necessary if applicable. Select one pre-weighed BHA sampling solution bottle for each impinger train for the sample run. Record the bottle ID and weight data on the field sheet. Place approximately one-third of the BHA sampling solution in each of the three impingers. An empty impinger may be placed prior to the three BHA impingers to condense the bulk of the moisture when testing high moisture sources. Furthermore, a silica gel or drying impinger may be used following the three BHA impingers.

2.5.7 Initial Leak Check (optional) – It is recommended that the sample probe and filter assembly be leak checked when the collection train is first assembled or after the filter is changed and before the system is brought up to operating temperature for the sample run.

2.5.8 Heated Probe/Impinger Train Leak Check – A leak check procedure must be conducted when all of the heated components have reached operating temperature (250°F ± 25°F). The leak check must include all of the components from the probe tip to the by-pass valve for the sample pump. A vacuum of at least 15 inches of mercury should be exerted on the system. A drop in vacuum of 1.0 inch of mercury over a two minute period indicates a leak that must be repaired. Results of the leak check must be recorded on the sample run field sheet.
***Caution:** Release the vacuum on the sample train at the probe tip.

Alternative leak check procedures may be used. If Method 5 type systems are used, the Method 5 leak check procedure may be used. For larger impinger trains with dry gas meters, a leak check conducted at the maximum vacuum (during the test run) must show a leak to be less than 4% of the sample rate during the test. Results of the leak check must be provided in the report.

2.5.8.1 Dual Impinger Train Leak Check Procedure – For systems using one heated probe and filter with two parallel impinger trains, care must be taken to isolate the two impinger trains during leak checks. If this is not done and there is a leak in the system, the impinger contents from one impinger train may be transferred through the filter housing to the other impinger train. Should this occur, the impinger contents for both impinger trains and the filter should be discarded and the sampling system reconstructed.

Two valves installed at the back of the heated filter box may be used to isolate the sample trains during leak checks. Alternative configurations can also be used but the sampling company must demonstrate that both impinger trains and the probe/filter box meet the leak check criterion.

2.5.8.2 Leak Check Troubleshooting – The presence of bubbles in the first impinger indicates a leak located between the probe and the first impinger. A leak between the impingers or behind the impingers will be indicated by aqueous solution being drawn up one of the impinger stems (flow direction is backwards through the system).

2.5.8.3 Post Leak Check – When an impinger train has passed the leak check, release the vacuum ***slowly*** at the probe tip to ensure that the aqueous solution remains evenly distributed between the impingers.

2.5.9 Sample Run Procedures – Prior to each sample run, verify that the probe and filter housing are both at operating temperature and all impingers are partially immersed in crushed ice and water.

2.5.9.1 Pre-Sample Run Flow Rate Measurement (single impinger train) – The required flow rate will depend on the size of the impingers and the amount of BHA solution used as specified in Section 2.2.5. The sample flow rate readings are obtained at the probe tip with the measurement system operated outside the source. The average of five flow rate readings will represent the pre-sample flow rate. Pre- and post-sample run flow rates are averaged for the sample run flow rate. Record the ambient temperature and pressure within the vicinity of the probe tip at the time of the measurement.

The measurement system should be operated only long enough to record the five flow rate measurements. First, turn the by-pass valve for the sample pump to "ambient" and turn the sample pump on, then switch the by-pass valve to "sample" in order to draw ambient air in at the probe tip. Obtain the required flow rate measurements and then return the by-pass valve back to "ambient." Keep the sample pump on for the remainder of the sample run.

If dry gas meters are used to determine sample volume, readings of 'delta H' across the orifice or an equivalent parameter must be reported to demonstrate relatively steady-state sample flow during the sample run.

2.5.9.2 Pre-Sample Run Flow Rate Measurement (dual impinger trains) – At the conclusion of a successful leak check for dual impinger trains, obtain the sample flow rate for both impinger trains independently. After the flow rates for the individual impinger trains are measured the combined sample flow rate from both trains is measured. The total sample flow rate should be within 10% of the sum of the independently measured trains.

If dry gas meters are used with each sample train to determine sample volume, readings of 'delta H' across the orifice or an equivalent parameter must be reported to demonstrate relatively steady-state sample flow during the sample run.

2.5.9.3 Pre-Sample Run Stack Flow Measurement – Verify that the source to be tested is operating at a reasonably steady state condition. Obtain the flow rate of the source gas at the stack test port using appropriate stack measurement methods. Other source gas parameters required must include stack gas temperature, moisture content, static pressure, and percent O_2 and CO_2.

2.5.9.4 Non-Isokinetic Sampling Single Point – Insert probe into the test port so that the probe tip is aligned perpendicular to source gas flow and situated at the sample extraction point. Check that the operating temperature of the probe and filter housing has not changed due to probe placement.

2.5.9.5 Start Sample Run – Start the sample run by switching the by-pass valves for the impinger sample pump(s) to "sample." Record the start time and observed sample flow rate through the impingers. This method does not specify a sample run time, but the run should be a minimum of 45 minutes. One hour runs are recommended. Three hour runs at reduced sample flow rates are reasonable for lumber kilns and other sources that have extended batch cycle times.

2.5.9.6 Verify Operating Parameters – At various intervals during the sample run, record the impinger flow rate observed, and vacuum gauge readings for the two gauges.

2.5.9.7 End Sample Run – At the end of the sample run, switch the sample pump by-pass valve for the impinger train(s) to "ambient." Record the time for the end of the sample run. Remove the probe from the stack test port to obtain the post-sample run flow rate.

2.5.9.8 Post-Sample Run Stack Flow Measurement – Obtain the flow rate of the source gas at the stack test port using appropriate stack measurement methods. Other source gas parameters required must include stack gas temperature, moisture content, static pressure, and percent O_2 and CO_2.

2.5.9.9 Post-Sample Run Flow Rate Measurement (single impinger train) – The sample flow rate readings are obtained at the probe tip with the measurement system operated outside the source. The average of five flow rate readings will represent the post-sample flow rate. Record the ambient temperature and pressure within the vicinity of the probe tip at the time of the measurement.

The measurement system should be operated only long enough to record the five flow rate measurements. Switch the by-pass valve for the sample pump to "sample" in order to draw ambient air in at the probe tip. Obtain the required flow rate measurements and then return the by-pass valve back to

"ambient." Keep the sample pump on in order to collect the sample line DI rinse.

2.5.9.10 Post-Sample Run Flow Rate Measurement (dual impinger trains) – At the end of the sample run, both impinger trains are attached to the heated filter housing and therefore the post-sample run flow rate can be measured at the probe tip. Switch the by-pass valves for both pumps to "sample" and record five flow rate measurements, then turn both by-pass valves back to "ambient." The average of these five readings will represent the post-sample run flow rate.

Next, obtain the independent flow rates for each impinger train. Verify that the sum of the independently measured flow rates for the two sample trains is within 10% of the total flow rate of the system.

2.5.9.11 Measurement System Sample Flow Rate Check – Verify that the difference between pre- and post-sample run flow rate measurements is within 20% (not applicable to sample systems with dry gas meters).

If the difference is greater than 20% for a given sample run, then examine the collection train and determine if the sample run is valid. A post-sample run leak check may be conducted in order to examine flow rate differences, but care is required to avoid loss of sample.

2.5.10 Sample Recovery Procedure

2.5.10.1 Rinse Sample Line – The sample line between the outlet of the filter housing and the first impinger must be rinsed with DI water. To accomplish this, disconnect the sample line at the heated filter box, turn the by-pass valve to "sample," and rinse the sample line with a small amount of DI water (approximately 5 mL for midget impingers). The rinse will be drawn into the first impinger (or the condenser if used).

2.5.10.2 Aqueous Sample Collection and Impinger Rinse – Verify that the ID of the original BHA sample bottle is documented correctly on the field sampling sheet for the impinger train and sample run type being processed. Transfer the BHA solution in the impingers to the original sample bottle. Rinse the three impingers with small amounts of DI water and add the rinse aliquots to the original sample bottle. If a condenser was used, empty the condensate into the BHA sample bottle along with the condenser's DI rinse.

Any loss of sample during the sample recovery and DI rinse must be estimated and that lost volume recorded on the field sheet and discussed in the sampling report. Care should also be taken to avoid contamination from airborne particles (e.g., MDF fiber) during sample recovery and DI rinse.

2.5.10.3 Hexane Impinger Rinse – Select a prepared hexane rinse bottle (Section 2.5.2) and record on the field sheet the bottle's ID and tare, pre-, and post-weights. If alternative means of tracking the hexane volume are used, record the appropriate information.

The aldehyde oximes formed by the reaction of the aldehydes with BHA are insoluble or slightly soluble in water. These oximes form an emulsion and also will float on the water surface and adhere to the impinger walls. To quantitatively capture the oximes, the impingers should be rinsed (washed) well with hexane. Begin the hexane rinse procedure by pouring the entire contents of the of hexane bottle into the third impinger. Wash the third impinger well. Transfer the hexane solution from the third impinger to the second impinger and wash the second impinger in the same manner. Repeat the process for the first impinger. The hexane rinse from the first impinger is then added to the BHA sample bottle. This rinse is used in the lab for the first extraction. Any spillage that occurs during this washing procedure must be estimated and recorded on the field sheet and discussed in the sampling report. Alternative procedures for measuring and tracking the aqueous sample volume and hexane volume are allowed. For example, the aqueous impinger catch and rinse may be measured or weighed in the field prior to the hexane impinger rinse.

If a condenser is used prior to the BHA impingers, the condenser is not rinsed with hexane, but is rinsed with DI water.

2.5.10.4 Post-Sample Weight – Obtain the post-sample weight of the bottle (this may be done in the laboratory) that will represent the weight of the bottle, the BHA aqueous sample, and the hexane rinse. Subtraction of the hexane rinse weight (mass) will provide the volume of aqueous sample that is needed to quantify methanol and phenol. This volume will be difficult to determine accurately if the weight (mass) of hexane in the sample is unknown. Note that hexane and water have different densities.

2.5.10.5 Sample Storage in the Field – The sample bottles must be stored at the test site on ice or in a refrigerator set at approximately 4°C. If the water samples are required to be shipped to the laboratory for analysis, pack the sample bottles in ice. **Be careful with frozen packs - they can freeze the water and cause breakage of sample bottles.** Also note that VOA vial type caps (with septa) can rupture if shipped by air. Solid caps with Teflon seals are suggested. Note that the samples contain hexane, and proper shipping procedures should be followed.

2.5.10.6 Sample Preservation – The samples should be refrigerated or remain on ice until processed.

2.5.10.7 Cleaning Impingers – After sample collection, all of the impingers must be cleaned. If the impingers are to be used again for subsequent testing, they must be cleaned in the field using isopropanol and methylene chloride or equivalent substitutes. The isopropanol is used first to remove any water or hexane remaining in the impingers. The methylene chloride provides a final wash and dries relatively rapidly so the impingers can be reused. Isopropanol and methylene chloride washes are not part of the sample and do not need to be analyzed. These materials should be disposed of properly. If the impingers are not reused during field testing, they should be cleaned using appropriate cleaning techniques for laboratory glassware prior to reuse.

2.5.10.8 Sample Storage in the Laboratory – All samples must be stored on ice or in a refrigerator (4°C) until analysis**.**

2.5.10.9 Timetable for Oxime Extraction and Sample Analysis – Extraction of the oximes must occur within 21 days of field sampling. The hexane extracting solution must be analyzed within 35 days of field sampling, and the aqueous fraction must be analyzed within 21 days of field sampling. If equivalency is demonstrated longer hold times can be utilized.

2.5.11 Sample Extraction Procedure

2.5.11.1 Sample Extraction and Separation of the Aqueous [AQU] and Hexane [HEX] Fractions

2.5.11.1.1 Sample Condition - The field samples should arrive at the laboratory in an ice chest or other container with ice or equivalent. The temperature of the samples should be between 0 and 10 degrees C. The samples should not be frozen. If the samples are not cold upon arrival at the lab, the test report must report the lack of proper shipping and the temperature of the samples upon arrival at the lab.

2.5.11.1.2 Sample Bottle Weight – Each sample bottle should contain the hexane rinse and associated aqueous sample solution. If the sample bottle containing all the sample has not been weighed, the bottles should be wiped dry and weighed, and the weight recorded. This step is necessary to quantify the methanol and phenol and insure that the full sample has been received.

2.5.11.1.3 Sample Extraction – After weighing the sample bottle, but before opening, shake the bottle vigorously for approximately 30 seconds. Pour the entire contents of the sample bottle into a properly sized separatory funnel. Cap and save the empty sample bottle. The hexane delivered with the sample will be used as the

first one-third of the total hexane volume used in the sample extractions. The total hexane volume used for the three extractions should be a minimum of 25% of the initial BHA solution volume (v/v). Shake the separatory funnel for 30 seconds and allow the hexane and water to separate. Drain the water fraction into a clean, labeled container. It is better to drain a little hexane into the water than to leave a little water in the hexane. Drain the hexane into the empty hexane container used in the field or a new tared container. Pour the water fraction back into the separatory funnel. Take the second-third of the hexane to be used in the extraction and pour it into the now-empty sample bottle. Shake vigorously for 20 seconds. Transfer this hexane solution to the separatory funnel. Shake and separate the fractions as before. Repeat for the third extraction, but the hexane used in this extraction will be "fresh" or "clean." All hexane fractions may be composited. The hexane and aqueous fractions are stored until analysis in separate labeled containers. The extracted (washed) aqueous sample contains methanol, phenol, and perhaps other non-hexane-extractable, polar compounds. The hexane solution contains the aldehyde oximes, perhaps ketone oximes, and other extractables.

The separatory funnels and other glassware should be cleaned between samples. An acetone rinse followed by a methylene chloride rinse and oven drying is sufficient. Other standard lab glassware cleaning practices are also acceptable. Care should be taken to avoid contamination with alcohols, ketones, or aldehydes. If acetone is an analyte, an equivalent solvent may be substituted.

2.5.12 [AQU] Aqueous Sample Lab Procedure

2.5.12.1 [AQU] Aqueous Sample Analysis – Prior to analysis, thoroughly review all calibration information (Section 2.6), all laboratory quality assurance procedures (Section 2.4), and make sure that all calibration standards, solutions, and reference standards are available or have been prepared (Section 2.3).

2.5.12.2 [AQU] GC/FID Procedure – Transfer an aliquot (2.0 mL) of the aqueous sample to an autosampler vial. Add 10 μL of the internal standard primary spike solution (30,000 mg/L cyclohexanol or 40,000 mg/L 2,2,2-trifluoroethanol) to each of the autosampler vials. (Other procedures that provide a standardized, equivalent internal standard concentration may also be used). Perform the analysis by direct aqueous injection into the GC/FID. If the concentration of an analyte is more than 10% above the calibrated range, the sample should be diluted and reanalyzed to measure the analyte concentration.

2.5.12.3 [AQU] GC/FID Operating Conditions – Table 2.7 in Section 2.8 provides GC/FID operating conditions. These conditions must be followed unless equivalency is demonstrated. Note that forest products industry exhausts contain large numbers of organic compounds, and the potential for coelution is substantial. Cryogenic conditions, the specified column, and other parameters have been developed to avoid co-elution of common forest products compounds. Elimination of cryogenic conditions or substitution of columns must not be done unless equivalency is established.

2.5.13 [HEX] Hexane Sample Lab Procedure – Prior to analysis, thoroughly review all calibration information (Section 2.6), all laboratory quality assurance procedures (Section 2.4), and make sure that all calibration standards, solutions, and reference standards are available or have been prepared (Section 2.3).

2.5.13.1 [HEX] GC/NPD Analysis – Transfer an aliquot (2.0 mL) of the hexane sample to an autosampler vial. Add 10 µL of the internal standard primary stock solution (20,000 mg/L nitrobenzene or equivalent compound and concentration) to each of the autosampler vials. (Other procedures that provide a standardized, equivalent internal standard concentration may also be used). Perform the analysis by direct injection into the GC/NPD. If the concentration of an analyte is more than 10% above the calibrated range, the sample should be diluted and reanalyzed to measure the analyte concentration.

2.5.13.2 [HEX] GC/NPD Operating Conditions – Table 2.8 in Section 2.8 provides GC/NPD Operating Conditions. These conditions must be followed unless equivalency is demonstrated. Few nitrogen or phosphorous containing organic compounds are present in forest products industry exhausts, therefore little potential for co-elution exists with an NPD detector. Typically the NPD chromatograms are very clean in the oxime region.

2.6 Calibration

2.6.1 Calibration and Standardization

2.6.1.1 [AQU] GC/FID Analyses

2.6.1.1.1 Notes – Assemble the GC/FID and establish the operating conditions outlined in Table 2.7. Once the GC/FID system is optimized for analytical separation and sensitivity, the same operating conditions must be used to analyze all samples, blanks, calibration standards, and quality assurance samples. Note for split/splitless injection ports constant injections of aqueous samples can cause water to build up in the system. This will cause the retention times to shift and the peaks to broaden. It is recommended that a bake-out of the system be performed after approximately 50 injections. This should consist of heating the injector to 250°C, the oven to 250°C, and the detector to 350°C for several hours.

2.6.1.1.2 Retention Times – Determine the retention times of the analytes by taking 2.0 mL of the mid-range calibration solution and adding 10 µL of the internal standard solution. This will result in concentrations of 150 mg/L of cyclohexanol or 2,2,2-trifluoroethanol in the autosampler vial. Inject 1.0 µL of this solution and determine the relative retention times of the analytes to the internal standard using Equation 2.7.

Equation 2.7

$$RRT_Z = \left[\frac{Rt_Z}{Rt_{IS}} \right]$$

Where:

RRT_Z = relative retention time of compound Z
Rt_Z = retention time of compound Z
Rt_{IS} = retention time of internal standard (cyclohexanol or 2,2,2-triflouroethanol)

2.6.1.2 [HEX] GC/NPD Analyses

2.6.1.2.1 [HEX] Extraction – All [HEX] samples to be analyzed by GC/NPD must be extracted from the aqueous impinger solution into hexane prior to analysis. This procedure is presented in Section 2.5.11. Extraction is necessary to remove the interference due to unreacted BHA and to quantitatively capture the oximes.

2.6.1.2.2 [HEX] Notes – Assemble the GC/NPD and establish the operating conditions outlined in Table 2.8. Once the GC/NPD system is optimized for analytical separation and sensitivity, the same operating conditions must be used to analyze all samples, blanks, calibration standards, and quality assurance samples.

2.6.1.2.3 [HEX] Retention Times – Determine the retention times of the analytes by taking 2.0 mL of the mid-range calibration solution and adding 10 µL of the internal standard solution. This will result in concentrations of 100 mg/L of nitrobenzene in the autosampler vial. Inject 1.0 µL of this solution and determine the relative retention times of the analytes to the internal standard using Equation 2.7.

2.6.1.3 [AQU] [HEX] 7 Point Calibration Curve - Prepare a seven-point calibration curve for each of the analytes by taking 2.0 mL of each calibration solution and adding the appropriate internal standard (Sections 2.5.12.2 and 2.5.13.1). The lower limit calibration standard must be 0.5 mg/L for the [HEX] samples and 0.4 mg/L for the [AQU] samples. The upper limit of the calibration standards should be 100 mg/L. Use of an internal standard for calibration is required. The calibration curve may be split into two curves, one for low concentration samples and one for the remainder. This may be done at the discretion of the analyst. It is strongly suggested that the analyst evaluate the need for splitting the curve relative to low and high sample concentrations.

2.6.1.4 [AQU] [HEX] Relative Response Factor - Calculate the relative response factor (RRF_A) for each analyte using Equation 2.8. If the relative standard deviation (RSD) of the average RRF_A is less than 15%, the calibration is acceptable. The average RRF_A can be used in all subsequent calculations. If the calibration does not pass the criteria, the calibration curve solutions must be reanalyzed and reevaluated. It may be necessary to perform instrument maintenance prior to reanalysis. If reanalysis also fails to produce a linear curve, new calibration standards must be prepared and analyzed.

Equation 2.8

$$RRF_Z = \left[\frac{A_Z}{A_{IS}} \times \frac{C_{IS}}{C_Z} \right]$$

Where:

RRF_Z = relative response factor of compound Z
A_Z = area of compound Z peak
A_{IS} = area of internal standard peak
C_Z = concentration of Compound Z injected
C_{IS} = concentration of internal standard injected

2.6.1.5 [AQU] [HEX] Calibration Verification Standard - Analyze and calculate the concentration of the mid-range calibration standard daily, prior to each sample set, using Equation 2.9. Calculate the percent recovery of the standard using Equation 2.10 to verify the calibration. In-house percent recovery control limits must be determined and are not to exceed ±15%. If the limits are exceeded, either prepare a new standard or perform instrument maintenance. If necessary, recalibrate the instrument.

Equation 2.9

$$C_Z = \left[\frac{A_Z \times C_{IS}}{A_{IS} \times RRF_Z} \right]$$

Where:

C_Z = concentration of compound Z in sample (mg/L)
A_Z = area of the compound Z peak in the sample
C_{IS} = concentration of the internal standard (mg/L)
A_{IS} = area of the internal standard peak
RRF_Z = relative response factor of compound Z

Equation 2.10

$$R = \left[\frac{C_M}{C_E} \times 100 \right]$$

Where:

R = percent recovery
C_M = concentration of analyte measured
C_E = concentration of analyte expected

2.6.1.6 [HEX] Aldehyde Calibration Standards – At this point in time the aldehyde oximes are not readily available commercially in small calibration grade quantities. Manufactured standard solutions may be available through a few suppliers. At this time, labs will (1) have to synthesize (manufacture) the oximes and prepare standard solutions from the synthesized neat oximes or (2) prepare or purchase standard solutions of aldehydes (and ketones) and derivitize these standards with a BHA solution. Instructions for synthesizing the oximes are provided in the appendix.

2.6.1.6.1 [HEX] Quantifying and Expressing Oxime Standards –The results from the chromatograms could be expressed as mg/L of aldehyde or mg/L of aldehyde oxime. Either method is acceptable, but all users will need to understand the basis or means of expressing the results. The least confusing way may be to develop the calibration curves based on the amount of aldehyde stoichiometric equivalent. For example, an addition of 3.386 grams of acetaldehyde oxime to one liter of hexane would provide an acetaldehyde oxime concentration of 3,386 mg/L but would provide an acetaldehyde stoichiometric equivalent concentration of 1000 mg/L. Labs should be clear about the reporting basis for their GC results.

2.6.1.7 [HEX] Stock Solution Made from Neat Oximes – If neat aldehyde or ketone oximes are manufactured or purchased, the calibration standards may be manufactured from the neat oximes using hexane as a solvent. Table 2.5 provides information for making a 1000 mg/L aldehyde stoichiometric equivalent stock solution for selected aldehydes.

Table 2.5 Standards from Oximes

Aldehyde	Aldehyde Molecular Weight	Oxime Molecular Weight	Milligrams of Oxime to Add to 100 mL of Hexane
Formaldehyde	30.05	135.15	450
Acetaldehyde	44.05	149.15	339
Acrolein	56.06	161.16	287
Propionaldehyde	58.08	163.18	281

2.6.1.7.1 [HEX] Oxime Calibration and Matrix Spike Solutions – Prepare calibration standard solutions by dilution of the stock solution made from neat oximes using syringes to measure the required aliquots of primary standard. Table 2.6 shows the required dilutions. Prepare matrix spike solutions by calculating the concentration of analytes desired and diluting the primary stock solution.

Table 2.6 Primary Stock Solution Dilutions

µL of Stock Solution to Add to 10 mL Volumetric Flask	Resulting Formaldehyde, Acetaldehyde, Acrolein, and Propionaldehyde Aldehyde Stoichiometric Equivalent Concentration (mg/L)
1,000	100
500	50
250	25
100	10
50	5
10	1
5	0.5

2.6.1.8 [HEX] Calibration Standards Made from Neat Aldehydes and Formalin – As an alternative to making or purchasing neat oximes, labs may prepare calibration standards from formalin and neat aldehydes. The neat aldehydes and formalin will be added to a BHA sampling solution (Section

2.3.8) where the oximes will be formed. Alternatively, purchased standard aldehyde solutions may be used. The oximes will be extracted from the solution with hexane providing a stock solution that can be diluted to provide standards.

Fill a 250 mL ground glass stoppered volumetric flask to approximately 240 mL with BHA sampling solution. Tare the flask. After the addition of each analyte, weigh and record the weight gain to the nearest 0.1 mg. Using a syringe or equivalent device, add 127 µL of acetaldehyde, taking care to inject the acetaldehyde directly into the water. In a like manner, add 119 µL acrolein, 250 µL formalin, and 126 µL of propionaldehyde. Once all the analytes have been added, fill the flask to the mark with BHA sampling solution. Allow to stand for 15 minutes at lab temperature or for one hour refrigerated. Shake the 250 mL volumetric flask and pour the contents into a properly sized separatory funnel for extraction. Add 40 mL of hexane to the 250 mL volumetric flask, cap, shake and then pour the hexane into the separatory funnel. Shake the separatory funnel for 30 seconds and allow the hexane and BHA solution to separate. Drain the BHA solution into a clean container. (It is better to drain a little hexane into the aqueous solution than to than to leave a little water in the separatory funnel.) Drain the hexane into a 100 mL volumetric flask and cap with a ground glass stopper. Pour the aqueous BHA solution back into the separatory funnel and add 30 mL of hexane. Shake and separate the fractions as before. Repeat with a third hexane extraction using 30 mL of hexane. After the third hexane fraction has been added to the 100 mL volumetric flask, use additional hexane to fill to the mark. Assuming 100% derivitization, 100% compound purity and exactly 37% formaldehyde in the formalin, this will result in individual oxime concentrations that are the stoichiometric equivalent of 1,000 mg/L of the corresponding aldehydes. Use the measured weight gains and actual compound purity to compute the exact analyte concentrations. This stock solution can be diluted as shown in Table 2.6 to provide standards.

2.6.1.9 Calibration Curve Checks – Section 2.4.1.2.2 requires a calibration check using a calibration verification standard. Section 2.4.1.2.5 requires a check by a second source or reference standard.

2.6.1.10 [HEX] [AQU] Calibration Frequency – It is critical that gas chromatography conditions remain stable. Calibration frequency will depend on the lab's practices, ability to control the chromatography conditions, and/or the ability to meet the calibration check standard criteria.

For this method calibration verification standards (Section 2.4.1.2.2) and a second source or reference standard (Section 2.4.1.2.5) are run at the beginning of each sample batch as a check on the calibration curve. The calibration verification standard must be evaluated for both compound concentration and response (peak area). The criteria are provided in Section

2.4.1.2.2. The calibration verification standard must be run prior to the sample batch, after every 10 source samples, and at the end of the sample batch. Each time it is run, the peak area and compound concentration must be evaluated relative to the QA criteria. Additionally, the peak area of the internal standard must be evaluated relative to the mean peak areas from the calibration curve. A 'new' calibration curve or recalibration is required if any of the calibration QA criteria are not met.

2.7 Calculations

2.7.1 GC Data Analysis

2.7.1.1 [AQU] [HEX] Relative Retention Time – The analytes are identified by comparison of their retention time relative to the internal standard established in the calibration to the relative retention time in the samples. The sample component relative retention time (RRT) should fall within ±0.01 RRT units of the RRT of the standard component.

2.7.1.2 [AQU] [HEX] Sample Concentration – Calculate the sample concentration, using the internal standard response factors established in Section 2.6.1.4, according to Equation 2.11. Use a dilution factor of 1 if no dilution is made and choose the proper correction factor based on the internal standard and hardware configuration used. Use a correction factor of 1 if no significant correction factor is found.

Equation 2.11

$$C_Z = \left[\frac{A_Z \times C_{IS} \times DF}{A_{IS} \times RRF_Z} \right]$$

Where:

C_Z = concentration of compound Z in sample (mg/L)
A_Z = area of the compound Z peak in the sample
C_{IS} = concentration of the internal standard (mg/L)
A_{IS} = area of the internal standard peak
RRF_Z = relative response factor of compound Z
DF = dilution factor

2.7.1.3 [AQU] [HEX] Dilution – If samples cannot be analyzed without dilution, the minimum measurement level (MML) must be adjusted to reflect the lowest dilution factor used by multiplying the MML by the dilution factor.

2.7.1.4 [HEX] Peak Summing – Some peak summing will be necessary as a result of the [HEX] GC/NPD analyses. Due to chemical structure, acetaldehyde oxime, acrolein oxime, methoxypropanone oxime, and propionaldehyde oxime each have two peaks. The main peak in each case is designated as A, and the lesser peak as B.

2.7.1.5 [AQU] [HEX] Data Review – The data are reviewed for accuracy of the identification, GC difficulties, interferences, and bias. Any difficulties are to be corrected prior to reporting analytical results.

2.7.1.6 [AQU] [HEX] Chromatogram Review – All the chromatograms are manually reviewed to confirm internal standard and analyte identification as well as the integrated areas. As part of this review, the analyst assesses whether or not the concentration is within the calibration range of the instrument. The analyst should determine whether dilution of the samples is required. Another tool that can be utilized to identify the analyte peaks is to overlay the sample chromatogram with the standard chromatogram.

2.7.1.7 [AQU] [HEX] Internal Standard Review – The internal standard area counts should be reviewed and added to a control chart. The in-house determined control limits should not exceed ±20% of the mean.

2.7.1.8 [HEX] Surrogates – If a surrogate standard is used, the surrogate standard concentration should be reviewed and added to a control chart. The in-house determined control limits should not exceed ±30% of the mean. Low recovery of the surrogate standard generally indicates that insufficient BHA solution was used to form the oximes. Should this be seen, the sample, or a dilution of the sample, must be re-extracted using larger quantities of BHA complexing solution.

2.7.1.9 [AQU] [HEX] Replicate Inconsistencies – Any inconsistencies between replicate analyses must be resolved (i.e., if an analyte is detected in one replicate and not the other) and attempts made to determine the reason for the inconsistencies.

2.7.1.10 [AQU] [HEX] Reporting – Generate a report that includes the internal standard recovery (based on area counts) and calculated concentration of the analytes.

2.7.1.11 [AQU] [HEX] Reporting of MML – Where analytes are not detected or are detected below the lowest calibration standard, report the MML.

2.7.1.12 [AQU] [HEX] Significant Figures – Report results in mg/L to no more than three significant figures.

2.7.1.13 [AQU] [HEX] QA Reporting – Report all blanks, duplicates or replicates, matrix spike recoveries, and the results of calibration verification standards and second source standards for each analytical batch of samples.

2.8 Tables, Diagrams, Flowcharts, and Validation Data

Table 2.7 GC/FID Operating Conditions for Aqueous [AQU] Analysis

Injection:	Purged Packed Injection Port
Purge Flow Rate:	Approx. 40 mL/min
Purge Time:	0.25 min
Injector Temperature:	110°C
Injection Volume:	1 μL
Injection Liner Size:	2 mm id
Syringe Rinse:	10 rinses with VOC free DI water
FID Detector Temperature:	275°C
H_2 Flow Rate:	Approx. 50 mL/min
Air Flow Rate:	Approx. 500 mL/min
Makeup Gas:	Nitrogen or Helium
Makeup Gas Flow Rate:	Approx. 25 mL/min
Carrier Gas:	Helium
Carrier Gas Flow Rate:	constant pressure mode to give 6 mL/min at room temperature, or use constant flow mode at 6 mL/min
Column:	J&W DB-624, 60 meters or longer x 0.53 mm id x 3 micron fused silica capillary column with 10 m deactivated fused silica guard column
Cryogenics:	On
Temperature Program °C:	
Initial:	5°C for 1 min
Ramp 1:	6°C/min to 90°C for 0 minutes
Ramp 2:	40°C/min to 150°C for 7 minutes
Ramp 3:	70°C/min to 250°C for 4 minutes
Retention Time Order:	Acetaldehyde, Methanol, Propionaldehyde, 2,2,2-Trifluoroethanol, Methyl Ethyl Ketone, Cyclohexanol
Cyclohexanol Retention Time:	22.081 min
Relative Retention Time:	Acetaldehyde - 0.336; Methyl Mercaptan - 0.356; Methanol - 0.367; Ethanol - 0.458; Propionaldehyde - 0.487; Acetone - 0.499; Dimethyl sulfide - 0.503; 2,2,2-Trifluoroethanol - 0.608; MEK - 0.672

Table 2.8 GC/NPD Operating Conditions for Hexane [HEX] Analysis

Injection:	Split (Split, 10:1, split flow 13.9 mL/min, total flow 22.9 mL/min)
Injector Temperature:	200°C
Injection Volume:	2.0 μL
Injection Liner Size:	4 mm id with glass wool packing
Syringe Rinse:	4 rinses with hexane
NPD Detector Temperature:	280°C
H_2 Flow Rate:	3 mL/min
Air Flow Rate:	60 mL/min
Carrier Gas:	Helium
Carrier Gas Flow Rate:	1.4 mL/min
Column:	RTX-200, 30 m x 0.25 mm id x 0.25 micron film capillary column with 10 m deactivated fused silica guard column
Cryogenics:	Off
Temperature Program °C:	
Initial:	55°C for 2 min
Ramp 1:	2°C/min to 105°C for 0 minutes
Ramp 2:	25°C/min to 280°C for 2 minutes
Retention Time Order:	Formaldehyde, Acetaldehyde B, Acetaldehyde A, Nitrobenzene, Acetone, Propionaldehyde A, Acrolein A, Propionaldehyde B, Acrolein B, MEK, Methoxy-propanone A, Methoxypropanone B
Nitrobenzene Retention Time:	14.700 min
Relative Retention Time:	Formaldehyde – 0.545 Acetaldehyde B – 0.853 Acetaldehyde A – 0.876 Nitrobenzene – 1.00 Acetone – 1.068 Propionaldehyde A – 1.123 Acrolein A – 1.148 Propionaldehyde B – 1.160 Acrolein B – 1.220 MEK - 1.317 Methoxypropanone A – 1.683 Methoxypropanone B – 1.704

Appendix

APPENDIX

Summary of Quality Assurance Procedures A1

Quality Assurance Configurations A2

Sampling Train Diagram A3

Example Calculation of Sample System Minimum Measurement Level (SSMML)
Based on a 0.4 mg/L Analytical Minimum Measurement Level (MML) for the GC/FID
(Aqueous Analysis) and 0.5 mg/L for the GC/NPD (Hexane Analysis) A4

Example Field Sheet – NCASI Method ISS/FP-A105.01 ..... A5

Oxime Synthesis Procedure A6

Bracketed Spike Recovery Example A7

Bracketed Spike Recovery Worksheet A8

SUMMARY OF QUALITY ASSURANCE PROCEDURES

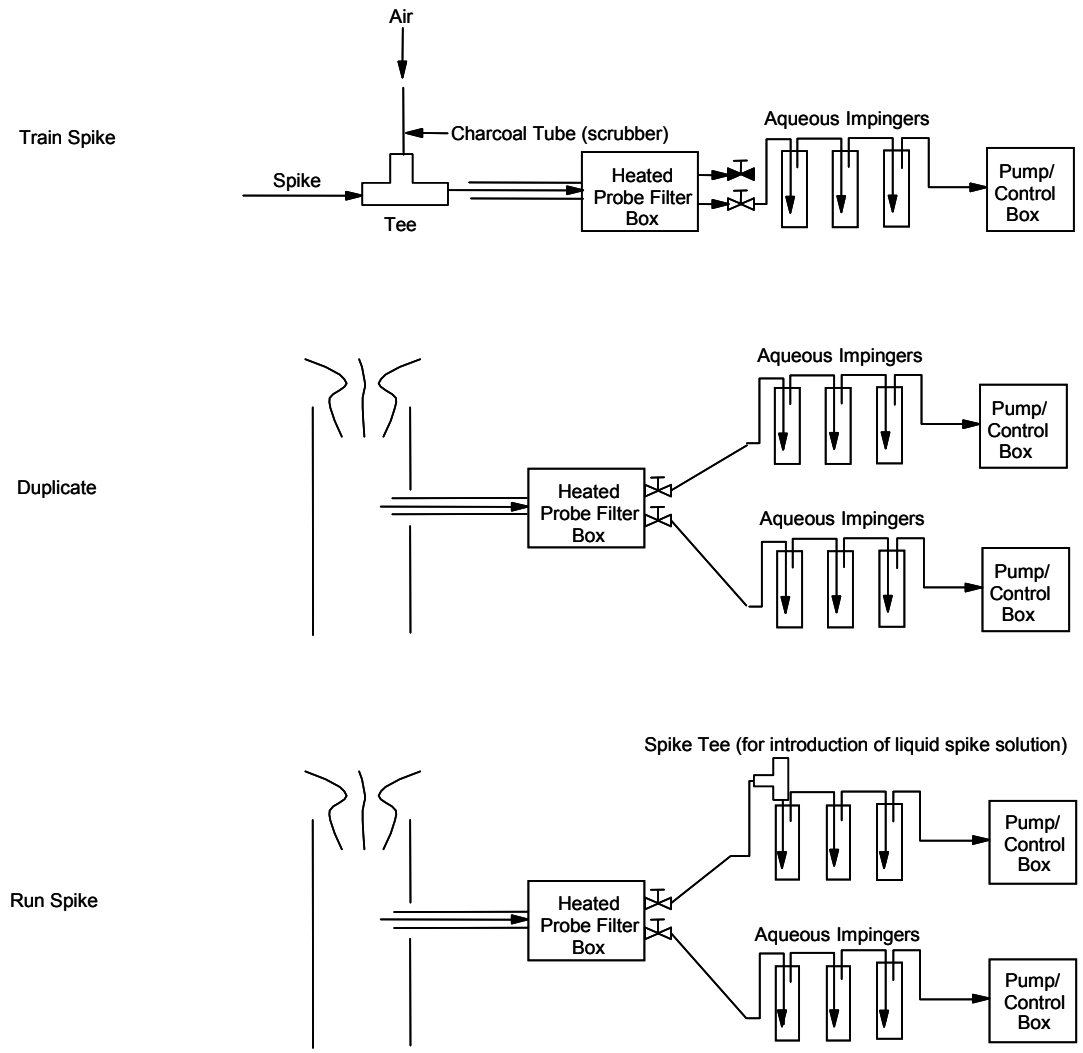
Field Quality Assurance Procedures

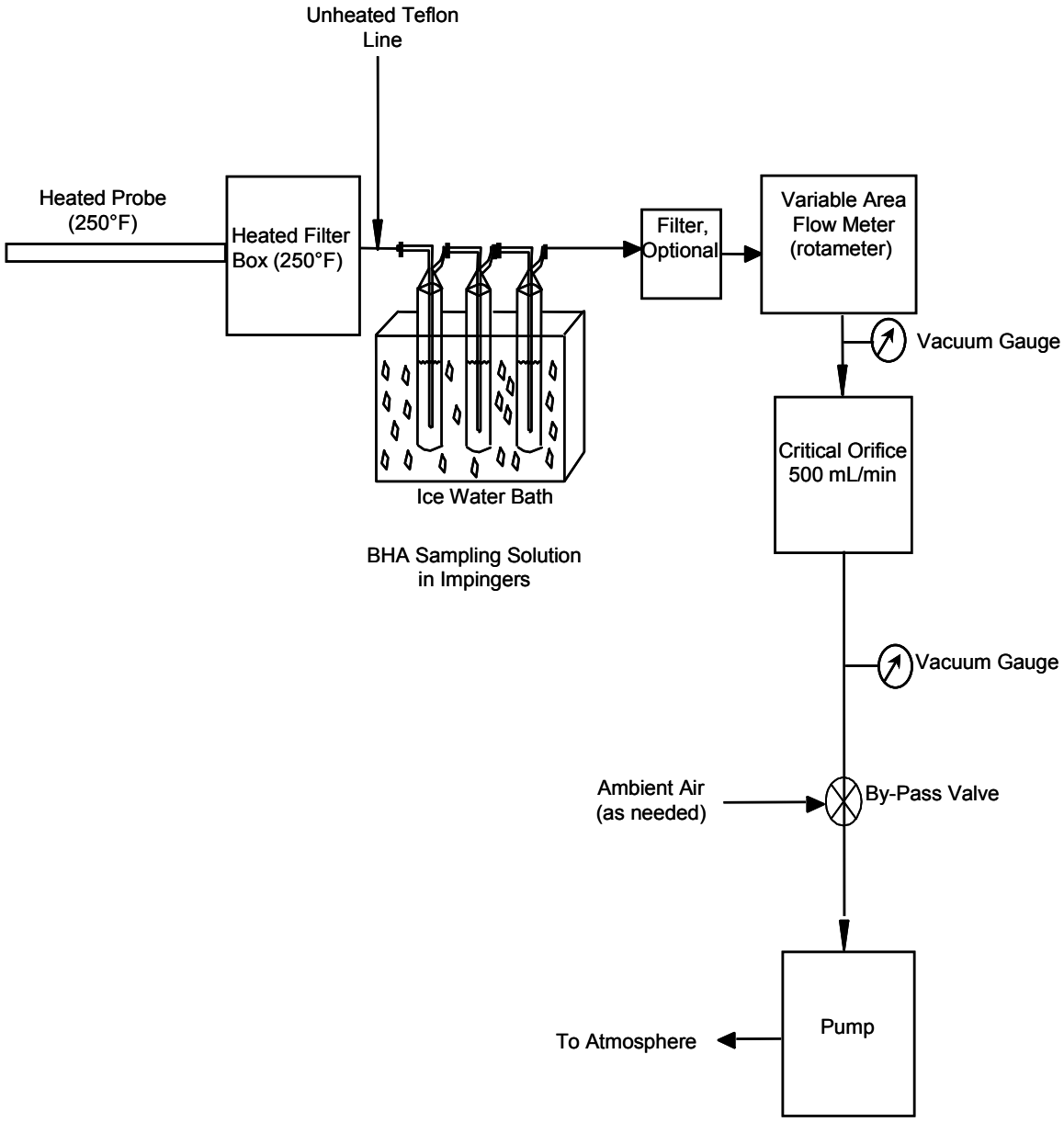
Procedure	Method Section	Criteria
Field Blank	2.4.2.2	None
Duplicate Sample Run	2.4.2.3	Table 2.3
Run Spike	2.4.2.5	Table 2.4
Train Spike	2.4.2.6	Section 2.4.2.6.3
Equivalent Spiking Level	2.4.2.1	Tables 2.1 and 2.2
Field Spike	2.4.2.4	None
Leak Check	2.5.8	Section 2.5.8
Sample Flow Check	2.5.9.1, 2.5.9.2, 2.5.9.9 and 2.5.9.10	Sections 2.5.9.11, 2.5.9.10, and 2.5.9.2

Laboratory Quality Assurance Procedures

Procedure	Method Section	Criteria
Lab Blank	2.4.1.2.1	Section 2.4.1.2.1
Calibration Verification Standard	2.4.1.2.2 and	Section 2.4.1.2.2
Laboratory Duplicates	2.4.1.2.3	Section 2.4.1.2.3
Matrix Spike Recovery (optional)	2.4.1.2.4	None
Second Source or Reference Standard	2.4.1.2.5	Section 2.4.1.2.5
Relative Response Factor	2.6.1.4	Section 2.6.1.4
Calibration Verification Standard	2.6.1.5	Section 2.6.1.5
Calibration Frequency	2.6.1.10	Section 2.6.1.10
Internal Standard Review	2.7.1.7	Section 2.7.1.7
Surrogates (optional)	2.7.1.8	Section 2.7.1.8

Quality Assurance Configurations





Sampling Train for NCASI Method ISS/FP-A105.01

EXAMPLE CALCULATION OF SAMPLE SYSTEM MINIMUM MEASUREMENT LEVEL (SSMML) BASED ON A 0.4 MG/L ANALYTICAL MINIMUM MEASUREMENT LEVEL (MML) FOR THE GC/FID (AQUEOUS ANALYSIS) AND 0.5 MG/L FOR THE GC/NPD (HEXANE ANALYSIS)

Assume:

(1) Sampling rate = 500 dry standard milliliters per minute for 60 minutes = 30 liters total.
(2) Three impingers with 25 mL each of BHA solution, plus 10 mL aqueous rinse, plus 5 mL of moisture from source (condensate) = 75+10+5 = 90 mL of aqueous impinger sample.
(3) Total hexane used in impinger rinse and extraction procedure = 30 mL.

Example Aldehydes SSMMLs

[(0.5 mg/L aldehyde) X (30 mL hexane) X (1000 μg per mg)] / (1000 mL per liter) = 15 μg of aldehyde. For the four aldehydes, 15 μg of aldehyde in 30 liters of gas sample volume yields the following concentrations in the air sample:

acetaldehyde	0.27 ppmvd
acrolein	0.21 ppmvd
formaldehyde	0.40 ppmvd
propionaldehyde	0.21 ppmvd

Example Methanol and Phenol SSMMLs

[(0.4 mg/L alcohol) X (90 mL aqueous sample) X (1000 μg per mg)] / (1000 mL per liter) = 36 μg of alcohol. For the two alcohols, 36 μg of alcohol in 30 liters of gas sample volume yields the following concentrations in the air sample:

methanol	0.90 ppmvd
phenol	0.31 ppmvd

Note that the sample system minimum measurement levels (SSMMLs) will vary according to the aqueous BHA solution volume, sample gas volume, and, for the aldehydes, the amount of hexane used in the extraction (alcohols are not affected by the hexane extraction). The above example is based on a sample flow to initial impinger ratio of 30,000 mL to 75 mL or 400:1. The method allows ratios from 200:1 to 4000:1. If lower methanol detection limit is desired, the BHA solution volume can be reduced or the flow rate through the impingers increased. Alternatively, the laboratory could double the aqueous injection volume (GC/FID) but, in this case, the lab **must** use a purged packed splitless inlet because of the volume of water. Doubling the injection volume would decrease the SSMML by 50%. Note that very high moisture sources will add water (condensate) to the impingers and increase the detection limits for the alcohols.

EXAMPLE FIELD SHEET
NCASI METHOD ISS/FP-A105.01

Mill Name: _____ City: _____

State: _____

Source Name: _____

Description of Location Sampled (include description of all control devices, quenches, air inlets, etc.):

_____

_____

Run Number: _____ Start Time: _____ Date: _____

Stop Time: _____

Measurement System Leak Check

Time: _____ Initial Measurement (in. Hg): _____

Time: _____ Final Measurement (in. Hg): _____

Leak Check Criteria - Must not lose more than 1 inch of Hg (vacuum) in 2 minutes. Meet Criteria? Yes No

Measurement System Flow Rates

Average 5 flow measurements below for Pre-Sample Flow (SF) = _____

1.	2.	3.	4.	5.

Average 5 flow measurements below for Post-Sample Flow (SF) = _____

1.	2.	3.	4.	5.

Average Sample Flow Rate _____ (indicate units)

Temperature Measurements

Ambient Temperature at Start of Run: _____ Time Recorded: _____

Ambient Temperature at End of Run: _____ Time Recorded: _____

Temperature Heated Probe at Start of Run: _____ Time Recorded: _____

Temperature Heated Probe at End of Run: _____ Time Recorded: _____

Temperature Heated Filter at Start of Run: _____ Time Recorded: _____

Temperature Heated Filter at End of Run: _____ Time Recorded: _____

Rotameter Readings

Time: _____ Flow: _____

Time: _____ Flow: _____

Time: _____ Flow: _____

Time: _____ Flow: _____

Time: _____ Flow: _____

Time: _____ Flow: _____

Quality Assurance Measures

Train Spike Conducted? Yes No

Duplicate Conducted? Yes No

Run Spike Conducted? Yes No

Field Blank Made? Yes No

Field Spike Made? Yes No

Notes

Field Sampling Data Sheet

OXIME SYNTHESIS PROCEDURE

General steps in making aldehyde-oxime oils:

1. For each aldehyde-oxime to be synthesized, add 5 grams of BHA-HCl to about 100 mL of water in a 150 mL beaker. (Scale up or down as needed.) Completely dissolve the BHA.

2. 5 grams of BHA-HCl is 0.0314 moles or 31.35 millimoles (5/159.6 = 0.0627). The stoichiometric amount of aldehyde for each 100 mL flask is:

   formaldehyde (not formalin) - 0.94 grams
   acetaldehyde - 1.38 grams
   propionaldehyde - 1.81 grams
   acrolein - 1.75 grams
   methoxypropanone - 2.76 grams

   Since residual aldehydes are undesirable, values less than the stoichiometric amount should be added. At the following amounts of aldehyde the theoretical yield of the aldehyde-oxime oil is provided.

Table in mL of Aldehyde

Compound	Amount Aldehyde Added (mL)	Theoretical Aldehyde-Oxime Oil Yield (g)
formalin	2.0	3.13
acetaldehyde	0.75	2.01
propionaldehyde	1.0	2.28
acrolein	1.0	2.42
methoxypropanone	2.0	4.20

3. While constantly stirring, add aldehyde to the BHA solution in the beaker using a syringe with a long needle. Add the aldehyde slowly and below the solution surface. A white, finely divided material will form initially. It is best to place this mixture in a separatory funnel overnight. The aldehyde-oxime oil will separate from the aqueous phase and can be removed with a Pasteur pipette or manipulated into a small vial with a minimum of aqueous phase retention.

4. Freeze the vial containing the oil. (The oil will remain liquid, but ice crystals will form if water is present.) Place a glass wool filter in a small funnel. Place the stem of the funnel in a small empty vial, and place this assembly in a beaker to hold the funnel vertical. Place this assembly in the freezer.

5. After freezing, quickly filter the oil through the glass wool filter. Freeze the vial a second time. If ice crystals are seen, the filtering procedure should be conducted until no ice crystals are visible.

6. Synthesized oximes should be kept in a refrigerator.

Example: Bracketed Spike Recovery

compound molecular weight	**acrolein** 56.06	**acetaldehyde** 44.05	**formaldehyde** 30.05	**methanol** 32.04	**propionaldehyde** 58.08	**phenol** 94.11
Low Level Run Spike (Low Level Spiked Sample Train)						
normal sample train sample volume (L)	30	30	30	30	30	30
spiked sample train sample volume (L)	33	33	33	33	33	33
concentration in normal train (ppmvd)	1.1	2.1	3.5	12.4	BDL	1.1
concentration in spiked train (ppmvd)	2.1	2.4	6.1	13.2	0.7	9
normal train (ug)	77.0	115.4	131.3	495.8	BDL	129.2
spiked train (ug)	161.6	145.1	251.6	580.6	55.8	1162.7
field spike (ug)	70	800	118	487	41	1200
Equivalent Spiking Level (ESL) (ppmvd)	0.91	13.23	2.86	11.07	0.51	9.29
ESL, % of actual source gas concentration	83%	630%	82%	89%	not calculated, normal train BDL	844%
Does ESL meet criteria?	yes	no	yes	yes	not calculated, normal train BDL	no
percent difference	17%	not calculated, ESL criteria not met	18%	11%	not calculated, normal train BDL	not calculated, ESL criteria not met
low spike recovery (%)	110%	not calculated, ESL criteria not met	91%	7%	not calculated, normal train BDL	not calculated, ESL criteria not met
High Level Run Spike (High Level Spiked Sample Train)						
normal sample train sample volume (L)	29	29	29	29	29	29
spiked sample train sample volume (L)	30	30	30	30	30	30
concentration in normal train (ppmvd)	1.3	1.9	4.1	13.2	0.5	BDL
concentration in spiked train (ppmvd)	13.6	15.3	34.3	100	20.4	9
normal train (ug)	87.9	101.0	148.6	510.2	35.0	BDL
spiked train (ug)	951.4	841.1	1286.3	3998.3	1478.6	1057.0
field spike (ug)	1050	800	118	4000	470	1200
Equivalent Spiking Level (ESL) (ppmvd)	15.01	14.55	3.15	100.04	6.48	10.22
ESL, % of actual source gas concentration	1155%	766%	77%	758%	1297%	not calculated, normal train BDL
Does ESL meet criteria?	no	yes	yes	yes	no	not calculated, normal train BDL
percent difference	not calculated, ESL criteria not met	666%	23%	658%	not calculated, ESL criteria not met	not calculated, normal train BDL
high spike recovery (%)	not calculated, ESL criteria not met	92%	960%	87%	not calculated, ESL criteria not met	not calculated, normal train BDL
Bracketed spike recovery	110%	92%	91%	7%	not calculated, low spike BDL, high spike did not meet ESL criteria	not calculated, high spike BDL, low spike did not meet ESL criteria
Alternate Value *			525%	47%		
Successful spike and recovery?	yes	yes	yes	no	no	no

* Section 2.4.2.5.3.2, Rule 3 allows the user to average spike recoveries or to use the spike with the smallest percent difference

WORKSHEET FOR DETERMINING THE SPIKE RECOVERY
QA PROCEDURE FOR WP ISS-FP-A105.01

Step 1: Calculate Equivalent Spiking Levels

$$ESL = mass_{field\ spike} \div MW \times 24.055\ L/gmol \div V_{run\ spike\ sample}$$

	Mass, µg	MW, g/gmol	$V_{run\ spike\ sample}$, dsL
LESL			
HESL			

$$LESL = \frac{(\quad\quad ug) \times 24.055 L/gmol}{(\quad\quad g/gmol) \times (\quad\quad L)} = \_\_\_\_\_ ppmvd$$

$$HESL = \frac{(\quad\quad ug) \times 24.055 L/gmol}{(\quad\quad g/gmol) \times (\quad\quad L)} = \_\_\_\_\_ ppmvd$$

Step 2. Sample Train Results

Spike Level	ESL, ppmvd	Normal Train (C_A), ppmvd	5 x C_A Ppmvd	10 x C_A ppmvd	Spike Train, (C_{ST})ppmvd
Low Bracket					
High Bracket					

Step 3. Spike Recovery Determination

- If using the bracketed run spike option, then the rules for the determining the spike recovery are:

Rule 1. Use this rule if both criteria are <u>YES</u>: (enter values)

Is LESL	>	$5xC_{A\ Low}$?	Yes/No
	>		

Is HESL	#	$10xC_{A\ High}$?	Yes/No
	#		

$$\text{If Yes, spike recovery} = \frac{[C_{ST\ High}(ppmvd) - C_{A\ High}(ppmvd)]}{HESL(ppmvd)} \times 100$$

$$= \frac{(\quad\quad ppmvd - \quad\quad ppmvd)}{\_\_\_\_\_ ppmvd} \times 100 = \_\_\_\_\_ \%$$

Rule 2. Use this rule if both criteria are <u>YES</u>: (enter values)

Is LESL	#	$5xC_{A\ Low}$?	Yes/No
	#		

Is HESL	>	$10xC_{A\ High}$?	Yes/No
	>		

$$\text{If Yes, spike recovery} = \frac{[C_{ST\ Low}(ppmvd) - C_{A\ Low}(ppmvd)]}{LESL(ppmvd)} \times 100$$

$$= \frac{(\quad \text{ppmvd} - \quad \text{ppmvd})}{\_\_\_\_\_\ \text{ppmvd}} \times 100 = \_\_\_\_\_\%$$

Rule 3. Use this rule if both criteria are <u>YES</u>: (enter values)

Is LESL	#	$5xC_{A\ Low}$?	Yes/No
	#		

Is HESL	#	$10xC_{A\ High}$?	Yes/No
	#		

$$\text{(3a) LESL Spike Recovery} = \frac{[C_{ST\ Low}(ppmvd) - C_{A\ Low}(ppmvd)]}{LESL(ppmvd)} \times 100$$

$$= \frac{(\quad \text{ppmvd} - \quad \text{ppmvd})}{\_\_\_\_\_\ \text{ppmvd}} \times 100 = \_\_\_\_\_\%$$

$$\text{(3b) Low Spike \%difference} = \text{ABS}\left|\frac{LESL(\text{ppmvd}) - C_{A\ Low}(\text{ppmvd})}{C_{A\ Low}\ (\text{ppmvd})}\right| \times 100$$

$$= \text{ABS}\left|\frac{\quad -}{\_\_\_\_\_}\right| \times 100 =$$

$$\text{(3c) } ESL_{High} \text{ Spike Recovery} = \frac{[C_{ST\ High}(ppmvd) - C_{A\ High}(ppmvd)]}{HESL(ppmvd)} \times 100$$

$$= \frac{(\quad \text{ppmvd} - \quad \text{ppmvd})}{\_\_\_\_\_\ \text{ppmvd}} \times 100 = \_\_\_\_\_\%$$

$$\text{(3b) High Spike \%difference} = \text{ABS}\left|\frac{HESL(\text{ppmvd}) - C_{A\ High}(\text{ppmvd})}{C_{A\ High}\ (\text{ppmvd})}\right| \times 100$$

$$= \text{ABS}\left|\frac{\quad -}{\_\_\_\_\_}\right| \times 100 =$$

Choices for Rule #3 Spike Recovery:

Choice 1: Use average of LESL Spike Recovery (3a) and HESL Spike Recovery (3c)

$$= \frac{\left[\left(high\right) \qquad \% + (low) \qquad \%\right]}{2} = \_\_\_\_\_\%$$

Choice 2: Use the ESL with the smallest *spike %difference* to calculate the spike recovery,

Which ESL Spike %difference is smaller? (circle one)

LESL Spike %difference (Step 3.3b) or HESL Spike %difference (Step 3.3d) ?

Then use (H or L)ESL Spike Recovery result from Step 3.3a or 3c = _____%

Which choice is going to be used? (circle on)

Choice #1 or Choice #2

Selected Spike Recovery from Choice # _____ for Step 3 = _____%

Rule 4.

Is LESL	>	$5xC_{A\ Low}$?	Yes/No
	>		

Is HESL	>	$10xC_{A\ High}$?	Yes/No
	>		

If the answer to both is "YES," then ESLs do not meet the criteria and spike recovery should not be calculated and reported. Report, instead, that the spike equivalent levels did not meet the Bracketed Spike Run Criteria.